# DEVELOPMENT OF SELF-ASSEMBLED POLYELECTROLYTE MEMBRANES FOR PERVAPORATION APPLICATIONS

by

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# Abstract

Electrostatic self-assembly is a simple, yet versatile and environmentally friendly technique. This technique has been widely used in different areas and recently it has also been used to make nano-structured separating layers for composite polyelectrolyte pervaporation membranes. Non-porous substrates are usually employed for electrostatic self-assembly depositions, but porous substrates have to be used for membrane applications because the composite membranes fabricated with non-porous substrates will have low permeation fluxes. When porous substrates were used to make composite membranes for pervaporation, it was reported that 60 double-layers were needed to get a membrane with suitable separation performance. The deposition of each double-layer needed about one hour, and the fabrication of reported self-assembled membranes with porous substrates was time-consuming and, from an industrial point of view, not practical.

The aim of this work was to make self-assembled composite membranes in a more practical way. The methodology used here is to find appropriate materials and suitable preparation conditions to make self-assembled composite membranes that have less than 10 self-assembled double layers but still have good performance for the dehydration of isopropyl alcohol (IPA)/ water mixtures by pervaporation.

A hydrolyzed polyacrylonitrile (PAN) ultrafiltration membrane is a permanently charged porous material. In this work, this porous material was, for the first time, used as a substrate for the fabrication of a composite self-assembled membrane. It was found that the hydrolyzed porous PAN membranes were good substrates for making self-assembled membranes for pervaporation.

In order to reduce the number of the depositions required for making composite membranes with suitable separation performance, a new deposition technique, concentration-changing deposition technique, has been developed. To obtain more extended conformations of polyelectrolytes to prevent them from going into the pores on a porous substrate, dilute deposition solutions were used for the first several depositions. After these first depositions, the pore size of the porous substrate had been reduced and

more concentrated solutions (but still dilute solutions) could be used for the subsequent depositions. By using more concentrated deposition solutions, the number of the polyelectrolyte coils adsorbed by the charged substrate was increased and the thickness of each deposited layer was increased. In this way, the total number of deposition layers needed for a good membrane would be decreased. It has been proved in this work that the number of deposition layers in a composite membrane can be reduced by using the concentration-changing deposition technique.

By selecting appropriate materials and by selecting proper preparation conditions, composite polyelectrolyte membranes with less than 10 self-assembled double layers have been successfully fabricated. The obtained membranes had good performance for the dehydration of IPA/water mixtures by pervaporation. The lowest number of double layers in a composite membrane was 2 and this composite membrane had both a high flux and a high selectivity. It was also found that using polyelectrolytes with high molecular weights and a porous substrate with fine pores were the prerequisites for making composite polyelectrolyte membranes with less than 10 self-assembled double layers, while using a polyelectrolyte pair with high charge densities was the prerequisite for making composite membranes with a high selectivity. The successful fabrication of polyelectrolyte membranes with less than 10 double layers makes self-assembled membranes more practical because self-assembled composite membranes can be easily fabricated.

The data reproducibility and the stability of self-assembled composite membranes with less than 10 double layers have been discussed in this work. Random defects in the self-assembled separating layer and low repeatability of thickness in the first several deposition layers are believed to be the major reasons for the relatively low data reproducibility of single composite membranes, while the conformation change of adsorbed polyelectrolytes is one of the reasons for the flux reduction of composite membranes with less than 10 self-assembled double layers. Though the flux reproducibility of single membranes is barely acceptable (relative error about 25%), the average fluxes of several membranes made under the same conditions show good reproducibility. All composite membranes with less than 10 self-assembled double layers,

from a structure point of view, were stable because the fluxes of polyelectrolyte membranes didn't increase as time passed.

The separation performance of the self-assembled composite membranes developed in this work is not as good as it was originally expected, but it is still better than that of commercial poly(vinyl alcohol) (PVA) membranes for the dehydration of IPA/water mixtures, which indicates that new self-assembled composite membranes could be used for practical dehydration of IPA. The flux of the self-assembled composite membrane with 2 double layers was two times higher than that of reported self-assembled membrane in the literature when an IPA/water feed mixture with 10.0 wt% of water was used at $60^{O}$C. The composite membrane with 2 self-assembled double layers is a high performance membrane for IPA dehydration.

The formation of a single self-assembled layer on a non-porous substrate has been studied, but nothing has been reported about the formation of a self-assembled multilayer on a porous substrate. Based on the separation performance of different self-assembled composite membranes made from different materials and at different fabrication conditions, a two-stage process is proposed to explain the formation of a self-assembled multilayer on a porous substrate. Polyelectrolyte molecules, in the first stage, will deposit on the non-porous portion of the surface of a porous substrate while polyelectrolyte molecules will go into and fill the pores on the surface of a porous substrate to change a porous substrate into a "non-porous" substrate. In the second stage, polyelectrolyte molecules will deposit on a "non-porous substrate" to form a multilayer. This process can also be used to explain the formation of a multilayer on a non-porous substrate.

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I also would like to thank my wife, Ming Xu, for her love, care and always being there with me through all the ups and downs. Without the support from my family, I could not finish this thesis.

**To**

**my wife Ming Xu**

**and my son David Yu Zhu**

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# CHAPTER 1

# INTRODUCTION

The separation of liquid mixtures is very important in industries. There are different technologies available for liquid separations and among them pervaporation is a relatively new technology. In a pervaporation process, a liquid feed mixture to be separated is brought into contact with the active and non-porous side of a membrane, while vacuum is applied at the downstream of the membrane, and a chemical potential gradient perpendicular to the membrane surface is established. Because different components in a liquid feed mixture have different solubilities and diffusivities in the active layer of the membrane, certain components in the feed mixture permeate through the membrane faster than others and thus separation takes place.

Pervaporation is a promising technology. It can be used to effectively separate azeotropes and close-boiling point liquid mixtures. Pervaporation is an energy-efficient process because only a small amount of permeate needs latent heat to be vaporized, while in a distillation process almost all components in the feed mixture undergo phase change repeatedly. In the early 1990's, some membrane technologists even optimistically believed that pervaporation would replace distillation to become a dominating process for liquid separation in the future. Almost a decade later, no signs show that this scenario can happen in the near future. Currently pervaporation technology occupies a small portion of the liquid separation market. It is hard to imagine that pervaporation will replace all

distillation, but it is certain that pervaporation will replace distillation or other liquid separation technologies in some specific applications.

In order to increase the market share of pervaporation for liquid separations, the performance of pervaporation membranes has to be improved to make this technology more economically competitive. Polyelectrolyte complexes or polyion complexes have been proved to be excellent membrane materials for solvent dehydration. Integral or composite membranes have been developed and tested for the dehydration of various aqueous organic mixtures on lab scales. Unfortunately, it is difficult to effectively control the membrane fabrication conditions to obtain polyelectrolyte complex membranes with consistent separation performance.

Electrostatic self-assembly is a simple, versatile and powerful technique. By using this technique, a chemically well-defined and self-assembled layer-by-layer polyelectrolyte complex film can be formed on a substrate. Because the driving force in an electrostatic self-assembly deposition is the electrostatic force between the charges on the surface of the substrate and the charges on the polyelectrolyte chains in the deposition solutions, there are no restrictions in the shape and size of base materials as long as they are suitably charged. Most polyelectrolytes are water-soluble, and water, in most cases, is the only solvent used in an electrostatic self-assembly deposition. Therefore, this technique is environmentally friendly. Though electrostatic self-assembly has been a very active research area for over 10 years and lots of potential applications of electrostatic self-assembly have been identified, using the self-assembly technique to make composite membranes, especially pervaporation membranes, is still not well explored and there are only a few publications about this application.

A pervaporation membrane needs to be selective enough for the components to be separated and to be as thin as possible to maximize the permeation flux. In addition, the membrane should also meet the mechanical strength and chemical resistance requirements. Usually, an integral pervaporation membrane cannot meet all these requirements, and thus composite membranes are preferred. A composite membrane consists of two layers: a separating layer where the separation takes place and a

supporting layer that provides the mechanical support to the separating layer. It is possible to use a highly selective material to make a non-porous separating layer and another chemical- and heat-resistant material to make a porous supporting layer. In this way, a composite pervaporation membrane can be tailor-made to have both a high selectivity and a high flux.

Polyelectrolyte complexes are highly hydrophilic, and polyelectrolytes can form nano-structured layer-by-layer complexes via an electrostatic self-assembly technique. A self-assembled polyelectrolyte multilayer can meet all the criteria required for the separating layer of a high performance composite membrane. Therefore, a self-assembled polyelectrolyte multilayer can be used as a separating layer to make a high performance composite membrane.

So far, most electrostatic self-assembly films are deposited on polished silicone wafers that are non-porous. However, for high performance composite membranes, porous supporting materials have to be used to reduce the transport resistance of the supporting layer. When the electrostatic self-assembly technique is used to make a self-assembled separating layer on a porous substrate, it is critical that all the pores on the substrate are completely covered. Otherwise the resulting composite membrane will have a poor selectivity.

A plasma-treated polyacrylonitrile (PAN) ultrafiltration membrane has been used in the literature as a supporting material to make composite polyelectrolyte pervaporation membranes with self-assembled separating layers for dehydration application [Klitzing and Tieke, 2004]. Unfortunately, the separation performance of reported composite polyelectrolyte membranes was much lower than originally expected. More importantly, the reported process for preparing self-assembled membrane is not suitable for practical applications because as many as 60 double-layer depositions are required to make a composite membrane with a reasonable permselectivity.

The objective of this work was to develop a more practical method to fabricate self-assembled composite membranes for dehydration applications. In order to meet this objective, the following tasks need to be done:

- Explore the feasibility of using hydrolyzed porous PAN membrane as a new porous substrate to make composite polyelectrolyte membranes with a self-assembled separating layer.
- Explore the possibility of reducing the number of double layers in a composite membrane while retaining its good selectivity by using concentration-change deposition technique.
- Develop a practical method to make self-assembled composite membrane with less than 10 double layers for the dehydration of isopropanol (IPA) /water mixtures by pervaporation.
- Study the effects of the parameters involved in membrane preparation on the separation performance of the membranes obtained.
- Study the reproducibility and the stability of the composite membranes with less than 10 double layers.
- The formation of a self-assembled multilayer on a porous substrate will be investigated to provide an insight into the membrane fabrication process.

In the following chapters, all these specific objectives will be addressed, and the research results and discussion will be presented along with some recommendations for future work.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Pervaporation process and pervaporation membranes

The term "pervaporation" was introduced at the beginning of the last century to describe the phenomenon that a liquid could evaporate through a non-porous barrier material, but some research work on pervaporation had actually started even earlier.

The first quantitative work on pervaporation was published in 1956 by Heisler [Koops & Smolders, 1991]. A cellulose membrane was used to separate water from an aqueous ethanol solution in this article and, since then, research on pervaporation has really taken off.

Although pervaporation had great potential for liquid separation, not much progress was made in the first half of the last century because at that time materials that could be selected for making pervaporation membranes were rather limited, and both the productivities and the selectivities of the membranes obtained were low. It was the rapid development of polymer science and engineering that led to many new materials and polymer modification techniques which helped the pervaporation technology grow. As a result, the first industrial pervaporation unit was built in France in the 1980's.

Over the past few years, both the number and variety of industrial pervaporation plants and the variety of solvents dehydrated with pervaporation technology have dramatically increased. Many pervaporation plants are now in operation, with more in development or pilot phases [Hilmioglu & Tulbentci, 2004].

A simple pervaporation system consists of a pervaporation module, a condenser and a vacuum pump, as shown in Figure 2-1. The liquid mixture to be separated is introduced to a pervaporation module and is separated into two streams through a pervaporation module: one is the retentate that contains the components rejected by the membrane and the other one is the permeate that consists of the components passed through the membrane. Inside the module, the feed mixture is in contact with one side (the active side) of the membrane. Some components will dissolve in the membrane and then diffuse through it. The permeate is removed as a low pressure vapor from the other side (the back side) of the membrane. The driving force for the separation is maintained by the vapor pressure differential (more strictly, the chemical potential differential) across the membrane. Different from distillation that utilizes the differences in volatilities of the components for separation, pervaporation relies on the differences in solubilities and diffusivities of the components in the membrane.

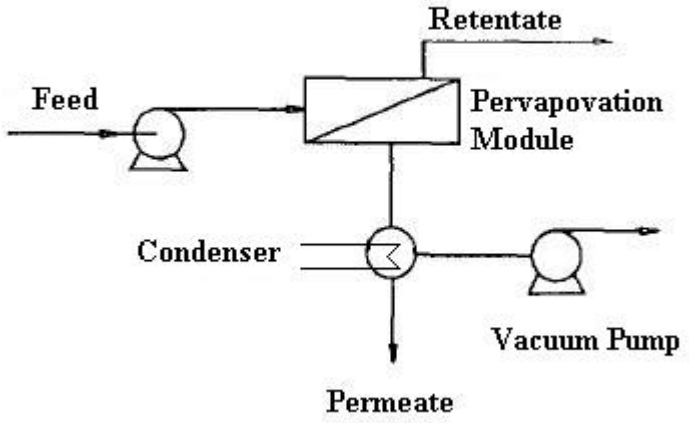


**Figure 2-1. Schematic of a typical pervaporation system**

Compared with distillation, pervaporation has the following advantages:

1. It is difficult to use distillation to separate the components in azeotropic mixtures or mixtures in which different components have almost the same volatility (i.e., close boiling points). To use distillation to break an azeotrope or to separate close-boiling-point mixtures, some entrainers have to be used. Pervaporation, on the other hand, can easily break an azeotrope or separate the components from a close-boiling-point mixture. Thus pervaporation can be used for the separation of mixtures that conventional distillation cannot separate effectively.

2. Pervaporation is an energy efficient process for liquid separation, especially when a feed mixture contains one component that is in low concentration and is more permeable than other components in the mixture. In a pervaporation process, only permeate needs latent heat to evaporate, while in distillation, almost all components in the feed undergo phase changes back and forth. As such, distillation consumes much more energy than pervaporation.

3. Pervaporation can be operated at a relatively low temperature, and this is important for the separation of some temperature–sensitive materials such as biomaterials. Also, the feed in pervaporation is usually at atmospheric pressure. It is easier to operate a pervaporation system than a distillation system.

4. A pervaporation system is small and compact, and the capital cost of a pervaporation system, relative to that of a distillation system, is low.

In spite of the advantages mentioned above, applications of pervaporation are very limited. Traditional liquid separation technologies are still dominant because of economic reasons. In order to make pervaporation more competitive, it is necessary to improve the engineering design of pervaporation, including module configuration, module fabrication and optimization of operating conditions and, more importantly, development of high performance membranes.

In addition to chemical resistance, thermal resistance and mechanical stability, a high performance pervaporation membrane needs to have a high productivity and a high selectivity.

The productivity of a pervaporation membrane is generally represented by permeation flux. The permeation flux (kg/m$^2$hr) of a membrane is determined by

$$J = \frac{Q}{At} \tag{2-1}$$

where Q is the amount of permeate collected (kg), A the membrane area (m$^2$), and t the time to collect permeate (hr).

The selectivity of a membrane can be expressed in different ways. Most commonly, the selectivity is expressed by the separation factor that, for a binary mixture system, is defined as:

$$\alpha_{ij} = \frac{x_i'' / x_j''}{x_i' / x_j'} = \frac{w_i'' / w_j''}{w_i' / w_j'} \tag{2-2}$$

where $x$ is molar fraction and $w$ weight fraction; $''$ represents the permeate side and $'$ the feed phase; $i$ is the component that is more permeable through the membrane than component $j$. For a fixed feed composition, the selectivity of a pervaporation membrane can be simply expressed by the concentration of the more permeable component in permeate. A high concentration of the more permeable component in permeate means a high selectivity of the membrane.

Pervaporation membranes generally have three different structures: homogeneous, integral asymmetric and composite membranes. Homogeneous membranes are easy to make, but the asymmetric and composite membranes offer the possibility of having a thin effective separation layer, which leads to a flux increase, while maintaining a high membrane mechanical strength. Since a single polymer usually does not have the optimum separation capability and mechanical stability at the same time, integral

asymmetric membranes can hardly be used for pervaporation effectively. Composite membranes, which are often produced from different materials, are widely used.

The solution-diffusion model is commonly used to describe the mass transport through a membrane. According to this mechanism, pervaporation consists of three steps: (1) sorption of permeate from the feed mixture to the membrane, (2) diffusion of permeate through the membrane, (3) desorption of permeate to the vapor phase [Feng & Huang, 1997]. Figure 2-2 is the concentration profile of the more permeable component in a pervaporation system with a composite membrane.

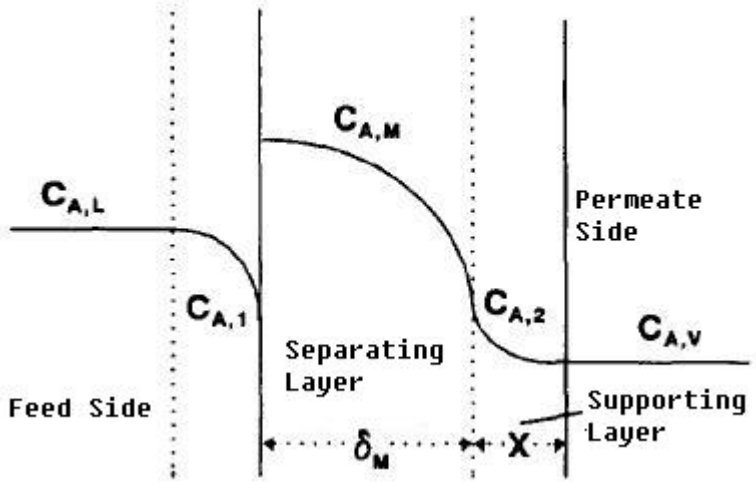


**Figure 2-2. Concentration profile of the more permeable component in a pervaporation system**

Pervaporation, theoretically, can be used for three types of separation: (1) the removal of a small amount of water from organics (dehydration application), (2) the removal of a small amount of organics from water (environmental application), and (3) the separation of organics from organics. Depending on the applications, three different kinds of pervaporation membranes can be distinguished [Lipnizki et al. 1999], that is, hydrophilic membranes, hydrophobic membranes and target-organophilic membranes.

To increase the productivity of a pervaporation membrane, the mass transport resistance of the membrane has to be decreased.

The total mass transport resistance in a pervaporation process comprises three parts: the resistance of the liquid boundary layer on the feed side, the resistance of the separating layer of the composite membrane, and the resistance of the supporting layer of the composite membrane. According to the resistance-in-series model, the total resistance in pervaporation can be written as:

$$R_T = R_L + R_{S1} + R_{S2} = R_L + R_M \qquad (2\text{-}3)$$

where $R_T$ is the total mass transfer resistance, $R_L$ the resistance of the liquid boundary layer, $R_{S1}$ the resistance of the separating layer of the composite membrane, $R_{S2}$ the resistance of the supporting layer of the composite membrane, and $R_M$ the overall resistance of the composite membrane ($R_{S1}$+$R_{S2}$). The resistance of the liquid boundary layer is related to the operating conditions and, therefore, can be reduced under suitable operating conditions. The total pervaporation resistance is mainly determined by the overall resistance of the membrane.

The resistance for permeate to pass through a porous substrate is much lower than through a non-porous substrate. The overall resistance of the membrane will be determined mainly by the resistance of the separating layer of the composite membrane if a porous substrate is used. Thus, a reduction of the resistance of the separating layer of a composite membrane will effectively increase the permeation flux through a composite membrane.

At steady state, the permeation flux of a component through the membrane can be described by the Fick's law:

$$J_i = -D_i \frac{dC_i}{dx} \qquad (2\text{-}4)$$

where $J_i$ is the permeation flux of component *i,* $D_i$ the diffusion coefficient of component *i* and $dC_i/dx$ the concentration gradient across the membrane.

The concentration dependence of the diffusion coefficient can be expressed by an exponential function shown below:

$$D_i = D_{i,0} \exp(r_i C_i) \qquad (2\text{-}5)$$

where $D_{i,o}$ is the diffusion coefficient of component *i* at zero concentration and $r_i$ is the plasticization parameter. Combining equations (2-4) and (2-5) and integrating across the separating layer, we get:

$$J_i = \frac{D_{i,o}}{r_i \delta}[\exp(r_i C_{i,1}) - \exp(r_i C_{i,2})] \qquad (2\text{-}6)$$

where $C_{i,1}$ and $C_{i,2}$ are concentrations at x=0 and x=δ, respectively, and δ is the effective thickness of the membrane.

Equation (2-6) shows that the permeation flux of a membrane is inversely proportional to the membrane thickness. To increase the permeation flux of a composite pervaporation membrane, we need to decrease the effective thickness of the separating layer of the composite membrane.

Equation (2-6) also shows that the permeation flux of the membrane is proportional to the diffusion coefficient. Increasing the diffusion coefficient of the permeate will also increase the productivity of the membrane. For a given feed mixture, increasing the diffusion coefficient means to use a membrane material with a high free-volume. It is not feasible to use a high free-volume material to make a highly selective membrane since the use of a high free-volume material as the separating layer will make the membrane obtained less selective.

The selectivity of a membrane can be separated into two terms qualitatively, that is, the solubility selectivity and the mobility selectivity.

$$\alpha = \alpha_s \alpha_m \quad (2\text{-}7)$$

The solubility selectivity can be increased by selecting a separating material that has a solubility parameter similar to that of the component to be permeated preferentially, while the mobility selectivity is dependent on several physical and chemical factors such as the size and shape of the permeating molecules and the molecular packing of the polymer used for making the separating layer. For a given mixture to be separated, the selectivity of membrane depends on the characteristics of membrane material.

Although poly(vinyl alcohol) (PVA)-based composite membranes supplied by Sulzer (formerly GFT) are the only commercial membranes for dehydration applications, the pervaporation separation performance of many other materials have been tested and compared in the literature. Figure 2-3 is a summary of ethanol dehydration performance of some typical pervaporation membranes. It appears that the dehydration performance of polyelectrolyte-based membranes (membrane sample 14 in Figure 2-3) is much better than that of the commercial PVA composite membranes. Polyelectrolyte-based membranes have the best performance among all membranes listed. Polyelectrolytes are excellent materials for making high performance composite membranes for dehydration applications.

**Table 2-1. Polymeric membranes used in Figure 2-3**

| No | Membrane | No | Membrane |
|---|---|---|---|
| 1 | Cellulose nitrate/polymethylacrylate | 2 | Poly(maleimide-co-acrylonitrile) |
| 3 | Chitosan | 4 | Quaternized poly(4-vinylpyridine-co-acrylonitrile) |
| 5 | Cross-linked PVA (GFT) | 6 | Polyhydroxymethylene |
| 7 | CMC/(0.8DS,$Na^+$) | 8 | Poly(allyl ammonium) chloride |
| 9 | Sulfonated polyethylene($Cs^+$) | 10 | Polystyrene sulfonated/PVA |
| 11 | Chitosan ($H_2SO_4$) | 12 | Alginic acid ($Co^+$) |
| 13 | Cross-linked Polyethylenimine complex | 14 | Poly(acrylic acid)-polyion |
| | | 15 | Cross-linked PVA ($100^OC$) |

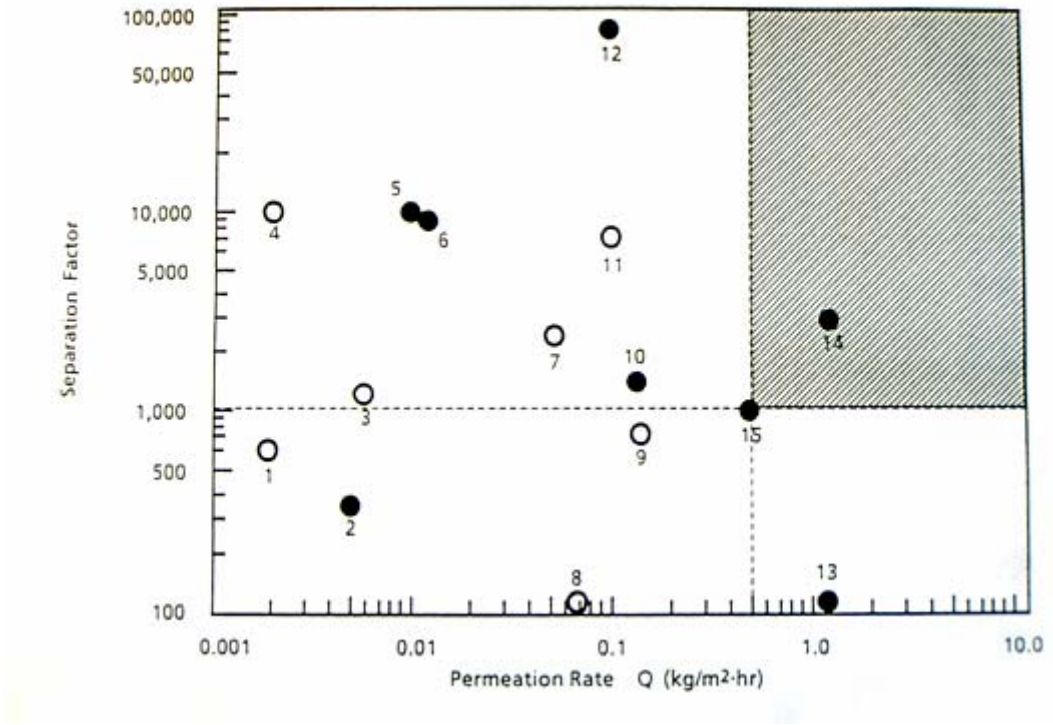


**Figure 2-3. Performance of ethanol dehydration membranes [Maeda & Kai, 1991]***

○: Feed ethanol 85-90 wt%　　●: Feed ethanol 82-95 wt%

* Reprinted from Pervaporation Membrane Separation Processes, R.Y.M. Huang (Ed.), Chapter 9, 391-435 (1991), with permission from Elsevier.

# 2.2 Polyelectrolyte complex membranes

Generally speaking, all membranes that contain at least one polyelectrolyte (polyion) as their component are polyelectrolyte complex membranes. According to this definition, there are two kinds of polyelectrolyte complex membranes. One contains a polyelectrolyte and a low molecular weight ion with an opposite charge. A

polyelectrolyte layer cross-linked with metallic oxide or metallic salt is a typical example of this kind of membrane. The other one contains two polyelectrolytes that have opposite charges. From membrane performance perspective, a polyelectrolyte complex membrane that contains a polyelectrolyte and a low molecular weight ion is not stable. As time passes, the membrane performance will decrease dramatically because the low molecular weight ion can be "washed" away in a pervaporation process. Polyelectrolyte complex pervaporation membranes consisting of two polyelectrolytes with opposite charges are more stable.

There are different ways to make polyelectrolyte complex membranes with two oppositely charged polyelectrolytes.

Symplex is the first generation of polyelectrolyte complex membranes. Schwarz et al. developed a Symplex membrane for pervaporation 15 years ago [1991]. The fabrication process of this membrane is, basically, two coating steps plus one mixing step. One layer of the first polyelectrolyte solution was coated onto a glass plate, and then one layer of the second polyelectrolyte solution with opposite charges was coated on top of the first solution layer. When these two polyelectrolyte solutions contacted each other, mutual diffusion (mixing) would take place under the concentration gradients. Precipitation occurred as the complexation between oppositely charged polyelectrolytes took place. After about 30 min of neutralization, the glass plate, together with the precipitation (membrane) formed on it, was placed into water, and the membrane began to stand apart from the glass plate. By choosing suitable polyelectrolytes, the membrane formed would not dissolve in water anymore. This method, though quite straightforward in principle, has several technical problems in practice.

It is very difficult to evenly coat the second polyelectrolyte solution layer on top of the first polyelectrolyte solution layer. When the second polyelectrolyte solution layer is spread on top of the first polyelectrolyte solution layer, the flat surface of the first solution layer, which is presumably distributed evenly, will be disrupted locally. Both the first solution layer and the second solution layer are not uniform in composition and thickness, which leads to variations in the final polyelectrolyte complex membrane.

There is no supporting material for the membrane formed this way. To meet the mechanical strength requirement, the membrane is usually rather thick (it could be more than 10 μm). But it is quite interesting that although this membrane is usually relatively thick, the reported flux of this membrane is significantly higher than that of the commercial PVA membrane.

The permeation flux of the polyelectrolyte membrane was shown to change substantially from time to time. The high flux of the membrane could be explained with the fact that the separating layer in the membrane (polyelectrolyte complexes) is much more hydrophilic than a cross-linked PVA layer. Another reason could be that in a Symplex membrane, there are numerous small and isolated voids. The thin polyelectrolyte complex layer forms a wall between these separated voids and keeps them together. When the permeate transports through the membrane, the transport resistance primarily comes from the thin polyelectrolyte walls. Therefore, in spite of a rather thick membrane structure, the mass transport resistance of the membrane is actually not high. This type of membranes had quite different fluxes in different publications, which could reflect the variation in membrane composition as well as in membrane morphologies. Some modifications had been made to improve Symplex membranes. For example, an attempt was made to transfer the wet polyelectrolyte complex layer to the top of a porous substrate. After drying under ambient conditions, an easy to handle, two-step polyelectrolyte composite membrane could be obtained. In this way, the thickness of a polyelectrolyte complex layer could be reduced and the mechanical strength of the membrane obtained could be improved significantly.

A Symplex membrane is formed by mutual diffusion of two polyelectrolytes with opposite charges. In order to form a uniform complex membrane, some polyelectrolyte molecules in one solution layer have to diffuse through the other solution layer to form a uniform complex layer. Can a polyelectrolyte molecule diffuse so far in the solution of another polyelectrolyte with opposite charges? Instinctively, it is impossible. Complexation is a rather fast process. It first takes place at the interface between the two oppositely charged solution layers, and a thin polyelectrolyte complex layer forms at the interface almost instantly when the two polyelectrolyte solutions with opposite charges

get together. It is therefore difficult for a polyelectrolyte molecule to diffuse through the polyelectrolyte complex layer already formed at the interface. If any polyelectrolyte molecules do penetrate the polyelectrolyte complex layer at the interface, a new and thin polyelectrolyte complex layer will form as soon as this polyelectrolyte molecule encounters a polyelectrolyte carrying opposite charges. As a result, a polyelectrolyte complex layer will get thicker and thicker and this will eventually prevent the mutual diffusion of oppositely charged polyelectrolytes. The diffusion of one polyelectrolyte in the solution of the other polyelectrolyte will be stopped. It is hard to imagine how a polyelectrolyte molecule can penetrate through the whole membrane thickness to form a uniform structure.

In addition to the "coating plus mixing" process, the "mixing plus coating" process also has been used for making polyelectrolyte complex membranes. Nam and Lee [1997] used chitosan as a polycation and poly(acrylic acid ) as a polyanion to make a polyelectrolyte complex membrane for pervaporation. They first mixed these two polyelectrolyte solutions together in different ratios, then they cast the mixed polyelectrolyte solutions on a polystyrene sheet and dried it at $30^{O}C$ in a convectional oven over 24 hr. The membranes obtained had a thickness of about 45-50 μm. From a fabrication point of view, it is hard to control this "mixing plus coating" process because when the two polyelectrolyte solutions with opposite charges mix together, precipitation will take place instantly even if the polyelectrolytes in the solutions are at very low concentrations. It is difficult to obtain a uniformly mixed polyelectrolyte solution and a uniformly mixed polyelectrolyte solution layer. As such, it is difficult to form a uniform polyelectrolyte complex membrane. This membrane was also found to have a lower flux and a lower separation factor than that of Sulzer's commercial PVA composite membrane. In fact, the flux of this membrane was rather low. For example, at $80^{O}C$ with a water-ethanol feed mixture containing 60.0 wt% of water (which represents a very high water concentration for ethanol dehydration process), the flux was still lower than 1.0 $kg/m^2hr$.

In order to improve the mechanical stability of Symplex membranes and to overcome the difficulties encountered in the fabrication of Symplex membranes, Marion et al. [1994] patented a modified process to make polyelectrolyte composite membranes.

This is a one-step, dip-coating process for making composite polyelectrolyte membranes on a porous substrate. PAN, polyetherimide, poly(vinylidene fluoride), and polysulfone porous membranes all can be used as the supporting substrates. Because the resulting membrane is a composite membrane and a supporting material provides the mechanical strength for the membrane, the thickness of the polyelectrolyte separating layer, in principle, can be reduced. The thickness of the polyelectrolyte complex separating layer alone was reported to be about 5-15 μm. The membrane was claimed to have both a high flux and a high separation factor. According to the patent, a porous substrate was dipped into the first polyelectrolyte solution continuously using a dip-coating roller so that a layer of the first polyelectrolyte solution was coated onto the surface of the porous supporting material. In the same way, a layer of the second polyelectrolyte solution with opposite charges would be coated on top of the layer of the first polyelectrolyte solution. Complexation took place when the polyelectrolytes with opposite charges contacted each other. After washing with distilled water, the composite membrane obtained was air-dried at 40-60$^{O}$C for 30 min.

A potential problem with this fabrication method is, in fact, similar to that in the fabrication of Symplex, that is, how to evenly coat the second polyelectrolyte solution layer on top of the first polyelectrolyte solution layer and how to form a uniform polyelectrolyte complex through the diffusion of one polyelectrolyte in another polyelectrolyte layer with opposite charge. It is difficult to control the thickness and the structure of the polyelectrolyte complex separating layer fabricated in this way. In fact, this method only provided a continuous process to make Symplex membranes but did not solve other problems that the old method had. So far, the dip-coating process is rarely used to make polyelectrolyte complex membranes.

Another problem is that the polyelectrolyte solutions can be coated on both sides of a porous membrane in a dip-coating process if a flat sheet substrate is used. Actually, the adsorption of polyelectrolyte on the backside of a porous membrane is easier than on the front side (that is the active side of a porous membrane) because a porous substrate usually has an asymmetric structure. When the polyelectrolytes are deposited on the backside, the permeation flux of the resulting membrane will decrease but the selectivity

may not increase. A simple dip-coating process is not suitable for making a high performance membrane.

Other attempts have also been made to make polyelectrolyte complex membranes. Child's research group [2002] has done some pioneering work in polyelectrolyte gel-filling membranes for pervaporation. Polyelectrolytes that have opposite charges interact with each other to form a gel. If the interaction takes place inside the pores of a microfiltration membrane, the resulting gel will fill the pores of the microfiltration membrane. The microfiltration membrane can provide the mechanical support, containment and protection for the polyelectrolyte gel, while the gel provides the passage for material transport. The gel is hydrophilic and the membrane so produced can be used for dehydration. Although the technique has been successfully applied for some applications, the separation performance of polyelectrolyte gel-filling membranes still needs to be improved for pervaporation application.

Iwatsubo et al. [2002] developed a method to make an asymmetric polyelectrolyte complex membrane. They cast a layer of polyelectrolyte (chitosan) solution on a glass plate. After being dried at room temperature, the polyelectrolyte layer was first immersed into a NaOH/ethanol solution to remove acetic acid that was used to adjust the pH of the chitosan solution and then washed with water. The thickness of the dry chitosan polyelectrolyte layer was about 15 μm. One side of the dry chitosan layer was brought into contact with a 0.03 monomol/L poly(acrylic acid) solution for different periods of time at different temperatures. When the poly(acrylic acid) solution contacted the chitosan layer, poly(acrylic acid) was assumed to diffuse into the chitosan layer because of the concentration gradient of the poly(acrylic acid) in the system. In the diffusion process, the interaction between chitosan and poly(acrylic acid) occurred and polyelectrolyte complex formed. An asymmetric polyelectrolyte complex membrane composed of chitosan and poly(acrylic acid) could thus be formed. It was claimed that this was a simple and convenient method to construct a highly water selective membrane without a considerable decrease in permeation flux. The thickness-normalized flux of this membrane seemed high because the membrane was relatively thick. The actual flux of the membrane, in terms of $kg/m^2hr$, was not high. The mechanical strength is also a

concern for this membrane because the complexation only takes place at the interface or near the interface, especially when high molecular weight poly(acrylic acid) is used. Cross-linking of the chitosan layer in this membrane may be necessary in order to maintain a reasonable stability.

A composite diffusion polyelectrolyte membrane has also been reported by Karakane et al. [1988, 1991], who coated a poly(acrylic acid) solution layer onto the surface of a polyethersulfone ultrafiltration membrane. The coated poly(acrylic acid), which could be cross-linked or un-cross-linked, was dried at 20$^{O}$C for 30 min. The solid poly(acrylic acid) layer, along with the polyethersulfone ultrafiltration membrane, was then dipped into a 2 wt% aqueous solution of polycation at room temperature for 12 hr to convert the poly(acrylic acid) layer into a polyelectrolyte complex layer. The composite membrane obtained was reported to have a high flux and a very high separation factor. When the water concentration in an aqueous ethanol feed was 5 wt%, the permeation flux was 2.17 kg/m$^2$hr (at 60$^{O}$C) and the separation factor was about 3000. These are the best results to date that have ever been reported about ethanol dehydration by pervaporation. This flux is, at least, 4 to 5 times higher than the fluxes reported by other researchers with other membranes under the same experimental conditions. The high separation factor could partially result from the characteristics of a polyelectrolyte complex. Because the polycation could not diffuse deep into the solid poly(acrylic acid) layer, the polyelectrolyte complex layer formed at the interface between the polycation solution and the solid poly(acrylic acid) layer was very thin, leading to a high flux. Though it was intended to convert all the poly(acrylic acid) into a polyelectrolyte complex matrix, it is actually impossible to do so because polycations could not diffuse through the polyelectrolyte complex layer that had been formed previously.

Similarly, Huang et al. [2000] used alginate salt as an active layer and a chitosan layer as a supporting layer to form a polyelectrolyte membrane on a porous poly(vinylidene fluoride) membrane. They called it a two-ply membrane. This membrane, in nature, is also a polyelectrolyte complex membrane though there is a difference between this membrane and Iwatsubo's membrane. In Iwatsubo's work, it was intended, by changing temperature and contact time, to increase the mutual diffusion between the

two oppositely charged polyelectrolytes while in Huang's work, the diffusion through the interface between two oppositely charged polyelectrolyte layers was less significant because the membrane was fabricated at room temperature. Even so, the molecular interpenetration and the complexation between oppositely charged polyelectrolytes at the interface did exist in a two-ply polyelectrolyte membrane. Thus, Huang's two-ply membrane can be considered as a special case or an extreme case of a composite asymmetric polyelectrolyte membrane made from a diffusion process. From a structural point of view, the two-ply membrane has a second polyelectrolyte layer on top of the first polyelectrolyte layer and both layers contain neutralized (at the interface) and un-neutralized polyelectrolytes. Neutralized polyelectrolytes formed a relatively stable complex network and no chemical cross-linking is necessary for neutralized polyelectrolytes. For un-neutralized polyelectrolytes, chemical cross-linking might be necessary to increase the stability of the two-ply membrane.

Polyelectrolyte complex pervaporation membranes can be prepared not only from currently existing polyelectrolytes but also from new polyelectrolytes that are obtained from common polymers by modification. By modifying non-polyelectrolyte PVA, Sun and Zou [2003] synthesized phosphatic anionic PVA and quaternary ammonium cationic PVA with various degrees of substitution and developed PVA–based polyelectrolyte membranes for dehydration applications. According to their results, some of the polyelectrolyte membranes they made had very good separation performance. For example, the polyelectrolyte complex membrane prepared by mixing phosphatic anionic PVA (degree of substitution 2.3%) and quaternary ammonium cationic PVA (degree of substitution 2.9%) in a weight ratio of 1:1 showed a permeation flux of 0.4 $kg/m^2hr$ and a separation factor of 2250 for the dehydration of ethanol/water mixture at $70^OC$ with a feed mixture containing 5.0 wt% of water.

As aforementioned, when two polyelectrolyte solutions containing opposite charges mix together, precipitation usually takes place instantly. Because of this, it is difficult to use the "mixing plus coating" method to make uniform polyelectrolyte complex membranes. But in Sun and Zou's work, no precipitation took place right away when the phosphatic anionic PVA solution was mixed with the quaternary ammonium

cationic PVA solution. Their explanation for this unique phenomenon is good compatibility between two polyelectrolytes with opposite charges and low degrees of substitution in the polyelectrolytes. Both quaternary ammonium cationic PVA and phosphatic anionic PVA were obtained by modifying PVA, and the chemical structure of these two polyelectrolytes in most place was the same and the compatibility between these two polyelectrolytes was very good. The degrees of substitution of both quaternary ammonium cationic PVA and phosphatic anionic PVA were rather low, which means the coulomb force was relatively weak and most of the repeat units in quaternary ammonium cationic PVA and in phosphatic anionic PVA were still vinyl alcohol units. The concentrations of ionized groups in the polyelectrolyte solutions were rather low and it took time for the oppositely charged groups to get together to form precipitation. Because there was no instant precipitation when these two oppositely charged polyelectrolyte solutions mixed together, the fabrication of this PVA-based polyelectrolyte membrane was very simple. The "mixing plus coating" method can be used to make PVA-based polyelectrolyte membranes. The quaternary ammonium cationic PVA solution was mixed with the phosphatic anionic PVA solution first and a rather uniform liquid mixture layer was obtained after coating. By drying this liquid mixture layer, a PVA-based polyelectrolyte membrane, which had a symmetric structure, was formed. It is easy to control this fabrication process to get membranes with repeatable separation performance. In this PVA-based polyelectrolyte membrane, the major interactions between polyelectrolytes were still the hydrogen bonds between PVA repeat units, and only a very small amount of ionized groups provided some extra interactions between the modified PVA chains. Therefore, the stability of this membrane could be an issue.

## 2.3 Electrostatic self-assembly technique and layer-by-layer structure

Self-assembly is the autonomous organization of components into patterns or structures without human intervention. Self-assembly could be at all scales [Whiteside and Grzybowski, 2002]. Self-assembly, in fact, is one of the few practical strategies for making nanostructures. There are different kinds of self-assembly techniques. Electrostatic self-assembly is a relatively new technique that was developed by Decher [1997] and his research group in the early 1990's. This technique is very simple, straightforward, versatile, powerful and environmentally benign.

Figure 2-4 illustrates an electrostatic self-assembly deposition process. The charged surface of a base material is exposed to a diluted polyelectrolyte solution that has opposite charges to the charges on the base material, and electrostatic interactions between the charges on the base material and the charges on polyelectrolyte chains in the solution will take place. To demonstrate an electrostatic self-assembly process, suppose the surface of the base material is negatively charged. When the surface of the base material is immersed in a dilute polycation solution, polycations will be adsorbed onto the negatively charged surface because of electrostatic attraction. Due to electrostatic repulsion, only one layer of polycation will be adsorbed onto the charged surface. Wash this surface with de-ionized water to remove any excess polycation molecules that are not adsorbed by the charged surface. Some of the charges on the adsorbed polycation molecules have been neutralized by the negative charges on the surface of the base material; some extra charges on the adsorbed polycation molecules have not been neutralized. These un-neutralized polycation charges make the new surface positively charged. This behavior is called charge overcompensation. Charge overcompensation is important and necessary because without charge overcompensation, an electrostatic self-assembly process could not proceed repeatedly and it would be stopped after a polyelectrolyte layer had been adsorbed onto the surface of the base material. Similarly, when the positively charged surface is then exposed to a dilute polyanion solution, one

layer of polyanion molecules will be adsorbed onto the previously formed polycation layer. The surface is washed again with de-ionized water to remove excess polyanions, and the surface now becomes negatively charged again. As a result, the new surface is ready for the next polycation deposition. Every single deposition forms one single polyelectrolyte layer that has a thickness normally between 0.5-8 nm. Every two consecutive depositions form a polyelectrolyte double-layer (a layer pair): one is a polycation layer and the other one is a polyanion layer. Consequently, the final multilayer prepared with the electrostatic self-assembly technique has an alternating polycation-polyanion layer structure or layer-by-layer structure. It is possible to control the overall thickness of the multilayer obtained by controlling the number of deposition cycles and/or by changing the deposition conditions (e. g., the pH's, the concentrations and ion strengths in the deposition solutions).

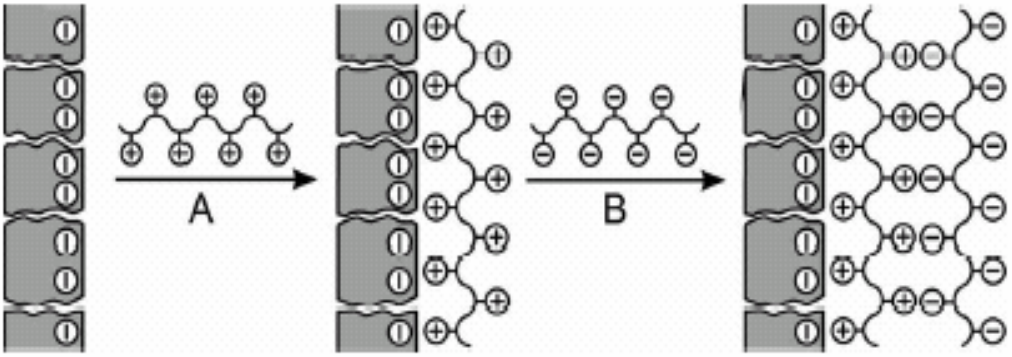


**Figure 2-4. The mechanism of electrostatic self-assembly depositions [Tieke et al. 2001]***

* Reprinted from Journal of Membrane Science, 181, Lutz Krasemann, Ali Toutianoush, Bernd Tieke, Self-assembled polyelectrolyte multilayer membranes with highly improved pervaporation separation of ethanol/water mixtures, 221-228 (2001), with permission from Elsevier.

Because the electrostatic self-assembly technique is based on electrostatic interactions that are universal interactions between oppositely charged objects, all charged materials can be used as starting base materials (supporting materials) to make self-assembled nano-structured multilayers, regardless of the size, the shape, and the topology of the surface of a charged substrate. Porous, non-porous, symmetric, asymmetric, organic (polymeric) or inorganic materials all have been tried for the depositions in the literature. Also, in principle, any kind of polyelectrolytes can be used to make self-assembled and nano-structured multilayer no matter whether the polyelectrolyte is strong or weak, with a high or low charge density, and with a high or low degree of ionization.

The electrostatic self-assembly technique, to some extent, has the ability to control the alignment of polyelectrolytes in a nano-structured film. The electrostatic self-assembly technique has become a very important technique in nano-technology and has been used in many areas. Nano-scale electronic circuits, nano-scale surface conducting polymers, surface light emitting polymers, light-absorbing polymers, color-changing polymers, flexible displays and protective coatings are just a few application examples. The electrostatic self-assembly technique can be used to effectively change the surface properties of current products and endow them with some new functionalities that would otherwise not be obtainable.

The electrostatic self-assembly technique usually uses water as the solvent, and no toxic solvent is involved. As such, this technique is not harmful to the environment. The electrostatic self-assembly technique, in principle, can make a defect-free nano-structured layer-by-layer film on a non-porous substrate because the defects formed in the previous layer, if any, could be self-repaired (self-cured) during the formation of the next layer. The overall nano-structured film fabricated with the electrostatic self-assembly technique will be defect-free if the number of layers in the film is large enough.

Because of the advantages mentioned above, the electrostatic self-assembly technique has attracted extensive attention over the past several years. Many efforts have been devoted to construct a nano-structured film on a non-porous silicon wafer and to

characterize its structure and stability. Dubas and Schlenoff [1999] listed the factors affecting the growth of a polyelectrolyte multilayer. They evaluated the dependence of the thickness of a polyelectrolyte multilayer on salt concentration, salt type, deposition time, and polyelectrolyte concentration. They used a strong polyelectrolyte pair poly(styrene sulfonate) / poly(diallyldimethylammonium chloride) for their study. It was concluded that for strong polyelectrolyte pairs, the film thickness was approximately proportional to the number of polyelectrolyte layers and the salt concentration. If the salt concentration (sodium chloride in the polyelectrolyte solution) was 0.5 mol/l, the thickness of 10 double-layers was about 120 nm. If the salt concentration was 1 mol/l, the thickness of 10 double-layers was about 250 nm. If there was no salt in the polyelectrolyte deposition solutions, the thickness of 10 double-layers was about 6 nm [Schlenoff and Dubas, 2001]. The salt concentration in the deposition solutions greatly affected the thickness of the resulting multilayer. It was found that an effective way to control the thickness of a multilayer built with strong polyelectrolytes was to add a salt into the polyelectrolyte deposition solutions.

Shiratori and Rubner [2000] studied the role that the solution pH played in the layer-by-layer structure formation of weak polyelectrolytes. Poly(acrylic acid) and poly(allylamine hydrochloride) were used for their study. Dramatically different polymer adsorption behavior was observed as one systematically increased (or decreased) the degree of ionization of a weak polyelectrolyte including transitions from a thick single adsorbed layer (ca. 8 nm) to a thin single adsorbed layer (ca. 0.4 nm) over a very narrow pH range. By controlling the pH of deposition solution, it is possible to control the thickness of an adsorbed polyelectrolyte layer from 0.4 to 8 nm. In addition, a control over the bulk and the surface composition of a resulting multilayer was readily achieved via simple pH adjustments. This research is very informative because an effective way was suggested to control the thickness of a polyelectrolyte self-assembled multilayer made from weak polyelectrolytes.

Dubas and Schlenoff [2000] studied the growth of a multilayer made with a weak polyanion (poly(acrylic acid)) and a strong polycation (poly(diallyldimethylammonium chloride)) as a function of the salt concentration and of the molecular weights of the

polyelectrolytes used. They found that the film thickness reached a maximum when the salt concentration was 0.3 mol/l and then decreased quickly. Pre-formed polyelectrolyte multilayers were shown to decompose rapidly in a solution as inorganic salt was added. A pre-formed multilayer made with high molecular weight polyelectrolytes would decompose completely when the pre-formed multilayer was exposed to NaCl solutions having concentrations higher than 0.6 mol/l. The apparent dissociation of multilayer polyelectrolyte complexes was attributed to the competition between polyelectrolyte/ polyelectrolyte ion pairs and polyelectrolyte/ external small molecular weight salt ions. For weak polyelectrolytes, the adjustment of solution pH could lead the polyelectrolyte to be completely ionized, partially ionized or non-ionized. As a result, for the polyelectrolyte multilayer composed of weak polyelectrolytes, great care has to be taken to keep the multilayer stable by controlling the pH value. According to their report, a multilayer having a thickness of 300 nm was obtained with poly(acrylic acid) /poly(diallyldimethylammonium chloride) (pH 5 and salt concentration 0.1 mol/l) in only 10 dipping cycles; the average thickness was 15 nm for each single deposition layer.

Decher [1997] gave an excellent review on the structure of polyelectrolyte multilayers. X-ray reflectivity experiments show that the actual structure of a polyelectrolyte self-assembled multilayer is not a strict layer-by-layer structure. There is no clear interface between the layers; one polyelectrolyte molecule chain in a specific layer can diffuse into the neighboring layers and overlap with the polyelectrolyte chains in the neighboring layers. Nevertheless, it is quite clear that the film fabricated with the electrostatic self-assembly technique does have an ordered structure.

The electrostatic self-assembly technique has been used for the making of gas separation membranes in the literature. Stroeve et al. [1996] made a gas separation membrane using spontaneous alternating self-assembly adsorption of cationic and anionic polymers on both porous and solid (non-porous) support materials. They used polyallylamine and poly(styrene sulfonate) as a polyelectrolyte pair and a porous polypropylene membrane and a solid polydimethylsiloxane membrane as substrates. The performance of the membranes was not very good for the separation of carbon

dioxide/nitrogen mixtures, but this did provide a new method to make gas separation membranes.

Sullivan and Bruening [2003] developed ultrathin, gas selective polyimide membranes using the electrostatic self-assembly technique. Different poly(amic acid) salts and poly(allylamine hydrochloride) were used as polyelectrolyte pairs to deposit on porous alumina supports, followed by heat-induced imidization to form polyimide composite membranes. Gas separation experiments showed that these membranes had very good separation performance. For the separation of oxygen and nitrogen, an ideal oxygen separation factor of 6.9 was achieved. For the separation of carbon dioxide and methane, an ideal carbon dioxide separation factor of up to 68 was reported. The electrostatic self-assembly thus provides a convenient way to prepare gas separation membranes with high fluxes and high selectivities on porous supports. One potential problem for making these gas separation membranes is that the imidization temperature is still too high if a porous polymeric supporting material is used.

The buildup of a multilayer is only achieved by repeated dip-coatings of a charged substrate in a polycation solution and a polyanion solution. This process is time-consuming. In order to speed up the formation of a layer-by-layer-structured multilayer, Schlenoff et al. [2000] tried to use sequential spraying of poly(styrene sulfonate) and poly(diallyldimethylammonium chloride) solutions on a supporting material to make a multilayer. A highly uniform multilayer was rapidly obtained over a large area. The morphology, uniformity, chemical composition and the properties of a sprayed multilayer were found to be virtually identical to those of a multilayer prepared by a dip-immersion process. Spraying is a fast method to make a layer-by-layer-structured multilayer.

# 2.4 Composite polyelectrolyte pervaporation membranes with layer-by-layer structure

The electrostatic self-assembly technique can be used to make a nano-structured polyelectrolyte complex film and polyelectrolyte complexes have been proved to be very selective for water in a pervaporation process. In principle, if a nano-structured polyelectrolyte multilayer fabricated with the electrostatic self-assembly technique is used as a separating layer to make a composite membrane for dehydration, the composite membrane should have very good separation performance. But is this feasible and practical for industrial applications? This is a relatively new application for the electrostatic self-assembly technique, and currently there are few published papers on this subject.

Kusumocahyo et al. [2002] used a non–porous symmetric membrane as a substrate to make a composite polyelectrolyte membrane. The symmetric non-porous substrate they used was a cellulose acetate membrane (12-14 μm in thickness). Polyallylamine and poly(acrylic acid) were used as the polyelectrolyte pair. The cellulose acetate membrane was first treated with plasma to make it negatively charged. According to their report, the cellulose acetate membrane, before electrostatic self-assembly depositions, was unable to separate an ethanol/water (90/10) mixture; but the separation factor was increased to about 80 after 3 double-layers had been deposited on the cellulose acetate membrane.

Meier-Haack et al. [2001], on the other hand, used non-porous asymmetric membranes as substrates to make composite membranes for dehydration applications. The substrate materials they used were polyamide-6 and modified polyamide-6. Modified polyamide-6 was prepared by reacting polyamide-6 with poly(α-methyl styrene-alt-ε-caproic acid-maleimide) in the melt state. When cast into an asymmetric membrane with a dense top layer (about 0.5 μm), the modified polyamide-6 membrane, compared with an un-modified polyamide-6 membrane, had more charged groups on the surface for

electrostatic self-assembly deposition. Different polyelectrolytes have been tried to get a dehydration membrane with good separation performance. It was found that when the composite membrane made from polyethylenimine, alginic acid salt and modified polyamide-6 substrate was used for the dehydration of an IPA/water mixture containing 30 wt% of water at $50^{O}$C, the separation factor was as high as 10,000 after 8 deposition cycles. Under the same conditions without polyelectrolyte depositions, the modified polyamide-6 base membrane had only a separation factor of less than 10. A composite self-assembled membrane with a high separation factor could also be obtained with polyethylenimine and poly(acrylic acid). However, all the membranes exhibited relatively low fluxes compared with Sulzer's commercial PVA composite membranes. The reason for this is quite obvious. A non-porous substrate was used for making these polyelectrolyte composite membranes and this non-porous substrate had a high resistance to the permeation, and the composite membranes obtained, thus, had low fluxes.

In order to increase the fluxes of composite membranes, asymmetric porous material was used as the supporting layer to make self-assembled composite membranes. Tieke and his research group [2001] have conducted a lot of work in this area. They used a porous PAN membrane supplied by Sulzer as the supporting material. Before depositions, the porous membrane was treated with oxygen plasma to make it negatively charged. The pore size of the porous PAN membrane was reported to be 20-200 nm. Different polyelectrolyte combinations have been explored. Figure 2-5 is a partial list of the polyelectrolytes they have used.

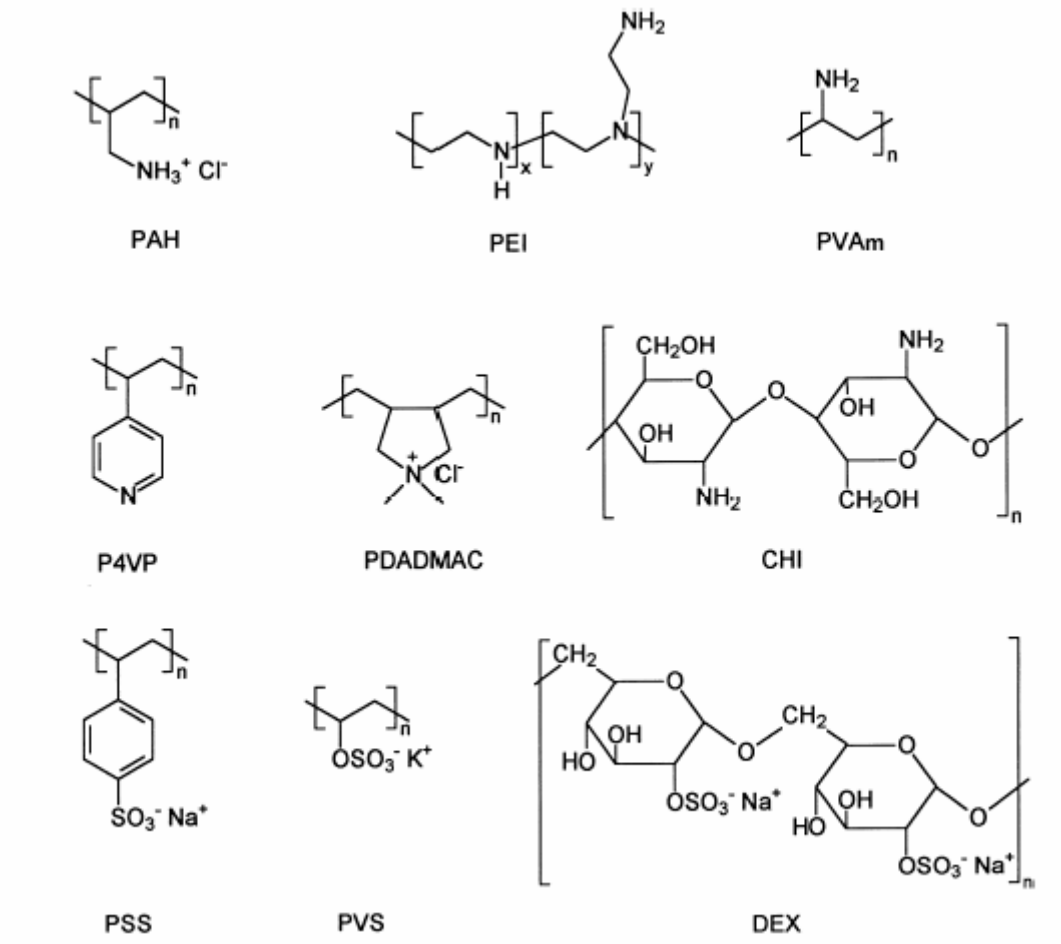


**Figure 2-5. Chemical structures of some polyelectrolytes used for making electrostatic self-assembled separating layers in the literature***

PAH: Poly(allylamine hydrochloride) PEI: Polyethylenimine

PVAm: Polyvinylamine P4VP : Poly(4-vinylpyridine)

PDADMAC :Poly(diallyldimethylammonium chloride) CHI :Chitosan

PSS :Polystyrensulfonate sodium salt PVS : Polyvinylsulfate potassium salt

DEX : Dextran sulfate

* Reprinted from Journal of Membrane Science, 181, Lutz Krasemann, Ali Toutianoush, Bernd Tieke, Self-assembled polyelectrolyte multilayer membranes with highly improved pervaporation separation of ethanol/water mixtures, 221-228 (2001), with permission from Elsevier.

Tieke and co-workers [2001] systematically investigated the effects of charge density of the polyelectrolytes used on the separation performance of the self-assembled membranes obtained. It was shown that the higher the charge density of the polyelectrolytes, the higher the water concentration in permeate and the smaller the flux. This can be easily explained in terms of the "cross-linking" degree of the polyelectrolyte separating layer. A higher charge density in a polyelectrolyte molecule means more potential physical cross-linking points in the polyelectrolyte complex formed by the polyelectrolyte. As the charge density of the polyelectrolyte increases, the "cross-linking" density of the polyelectrolyte network will increase. As a result, the flux of the resulting membrane will decrease while the selectivity of the membrane will increase. The research conducted by Tieke's group also showed that these polyelectrolyte membranes exhibited good stabilities. Even after the membrane had been used for 3 months, the membrane still had almost the same separation factor as a fresh membrane and almost the same flux. Generally speaking, the fluxes of the composite membranes made by Tieke's group are low for the dehydration of ethanol. These fluxes are much lower than expected based on the potential dehydration capability of a polyelectrolyte complex and on the thickness of a self-assembled separating layer. It is even lower than that of Sulzer's commercial PVA membrane that is made with a solution-cast technique. Possible reasons for the low flux of these composite membranes are that the pore size of the supporting material (20-200 nm) is too large whereas the molecular sizes of the polyelectrolytes are too small. When the coil sizes of the polyelectrolytes in the deposition solutions are relatively small compared with the size of the pores on a porous substrate, polyelectrolytes will go into the pores during depositions. If polyelectrolytes go into the pores, the polyelectrolyte separating layer formed can be much thicker than what will be formed on a smooth and non-porous surface. For polymers with molecular weights between $10^5$ and $10^7$, the radii of gyration of the polymers in good solvents are between 10 and 120 nm [He et al. 1990]. Most of the polyelectrolytes used in the literature for making self-assembled separating layers have molecular weights in the order of $10^5$ or less and therefore radii of gyration less than 50 nm. These polyelectrolytes would go into the pores that had pore size between 20 and 200 nm. Although it was claimed that there was no polyelectrolyte going into the substrate pores [Klitzing and Tieke, 2004], the

penetration of polyelectrolyte molecules in these pores was inevitable. When polyelectrolytes did go into the pores, it was difficult to obtain a nano-structured polyelectrolyte separating layer on a porous substrate. And if a separating layer in a composite membrane is thick, the flux of the composite membrane will be low. The dehydration performance of the composite membranes made by Tieke's group is shown in Fig. 2-6.

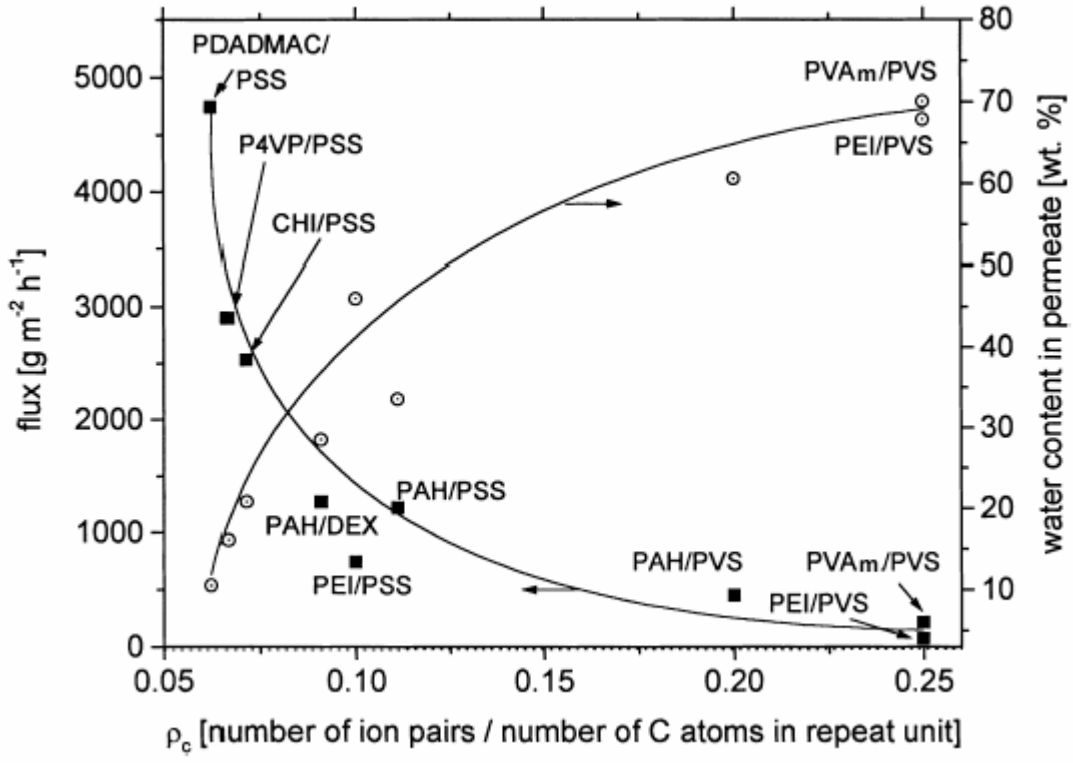


**Figure 2-6. Dependence of flux and water content in permeate on the charge density of polyelectrolyte complex (Tieke et al. 2001)***

60 double-layer membranes, feed containing 6.2 wt% of water,
feed temperature 58.5°C, See Figure 2-5 for abbreviations.

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For practical applications, the separation performance of Tieke's composite polyelectrolyte membranes needs to be further improved. More importantly, the process used by Tieke's group to make the composite polyelectrolyte pervaporation membranes is too time-consuming. For example, the deposition of each polyelectrolyte layer pair took about 60 min, and usually 60 layer pairs were needed to make a separating layer for a composite membrane with the separation performance given in Figure 2-6. Thus the total time for making a composite membrane, without counting the washing time between depositions and the time for substrate preparation, would be 60 hours. Clearly, the number of depositions needed for making a polyelectrolyte composite membrane has to be greatly reduced to make this membrane practical.

The literature review had showed that it was necessary to explore the possibility of making polyelectrolyte composite membranes with much fewer layers while retaining a good separation performance. Therefore, the objective of the present thesis work was to develop a practical method to make composite self-assembled polyelectrolyte membranes with reduced double layers and with good separation performance for the dehydration of IPA/water mixtures.

# CHAPTER 3

# PRELIMINARY STUDY ON POLYELECTROLYTE COMPOSITE MEMBRANES WITH REDUCED SELF-ASSEMBLED LAYERS*

## 3.1 Background

Composite polyelectrolyte pervaporation membranes using a porous material as supporting layer have been reported. At least 50 self-assembled polyelectrolyte double layers were needed to make a separating layer for a composite polyelectrolyte pervaporation membrane with acceptable separation performance [Toutianoush & Tieke 2002]. Actually in most of the reported work, 60 self-assembled polyelectrolyte double-layers were used for the separating layers of composite polyelectrolyte pervaporation

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membranes. The separation performance of these composite polyelectrolyte pervaporation membranes was not as good as previously expected, while the process of making the composite pervaporation membranes with self-assembled separating layers was too time-consuming to be used for practical applications. To develop self-assembled composite polyelectrolyte membranes for practical use, the process for fabricating these composite membranes has to be greatly simplified. To be more specific, the number of the deposition cycles required or the number of the self-assembled double layers needed in a composite polyelectrolyte membrane has to be reduced from 60 to a more reasonable number.

In order to develop a self-assembled polyelectrolyte membrane with reduced number of double layers, a separating layer with reduced number of double layers needs to be developed. While in order to make a separating layer with reduced number of double layers, it is necessary to understand why the self-assembled separating layers in the composite membranes reported in the literature needed about 60 double layers to have good separation performance.

A self-assembled separating layer in a composite membrane for pervaporation should be a non-porous multilayer because a liquid-liquid separation needs a non-porous membrane. If a non-porous substrate is used for making a self-assembled separating layer, every deposition can form a non-porous layer on the substrate and every deposition will contribute to the improvement of the separation performance of the final membrane. Only few depositions will be enough to give the final membrane good separation performance. When a non-porous substrate is used for making a composite membrane, polyelectrolytes with any molecular weights, in principle, can be used to form non-porous deposition layers.

If a porous substrate is used for making a self-assembled separating layer, the selection of materials is a bit more complicated. Both the pore size of the substrate and the molecular sizes of the polyelectrolytes are very important. If the pore size of the substrate is larger than the molecular sizes of the polyelectrolytes, porous polyelectrolyte deposition layers may be formed in the first several depositions because some

polyelectrolytes will enter the pores and pores will form on deposition layers. When the polyelectrolyte molecules go into the pores, they will be adsorbed by the oppositely charged inner surface of the pores and the pore size on the porous substrate will be reduced. When the pores become too small that polyelectrolyte molecules cannot enter them, polyelectrolyte molecules will form a non-porous deposition layer on the porous surface. So the function of the initial depositions on a porous substrate with large pores is to fill the pores and thus to reduce their size. These depositions do not contribute much to the improvement of the separation performance of the final membrane, but without these depositions it is impossible to make a self-assembled composite membrane with a porous substrate. The number of these filling depositions strongly depends on the size of the pores and the molecular sizes of the polyelectrolytes. Because of these filling depositions, the total number of depositions will be large if a porous substrate with a large pore size is used to make a self-assembled composite membrane.

If the pore size of the substrate is much smaller than the molecular sizes of polyelectrolytes, polyelectrolyte molecules will have a slim chance to go into the pores. Every deposition on the porous substrate will improve the separation performance of the membrane obtained. In this case, the deposition on a porous substrate is similar to that on a non-porous substrate and few depositions will give the final membrane good separation performance. The total number of depositions needed in a membrane is low. So the number of double layers can be controlled by selecting a porous substrate with fine pores and by selecting polyelectrolytes with high molecular weights.

The pore size of the substrate used for making a self-assembled membrane directly affects the number of depositions needed for a membrane. The pore size of the substrate used in the literature to make self-assembled membranes was reported to be between 20 to 200 nm. Obviously this porous substrate had not only a large average pore size, but also a wide pore size distribution. In order to get proper separation performance from a composite polyelectrolyte membrane, all the pores on the porous substrate used have to be totally sealed by self-assembled double layers. The larger the pore size, the more filling depositions are needed to change a porous substrate into a “non-porous” one. The total number of depositions needed for a self-assembled composite membrane

includes the number of filling depositions and the number of performance-improvement-depositions. Therefore, when the pore size of a porous substrate is increased, the number of filling depositions will be increased and the total number of depositions needed for making a self-assembled membrane will be increased too.

**Table 3-1. Molecular weights of polyelectrolytes used for making composite polyelectrolyte pervaporation membranes [Krasemann et al. 2001]**

| Polyelectrolyte | Molecular Weight |
|---|---|
| Poly(allylamine hydrochloride) | 9,600 |
| Polyvinylamine | 100,000 |
| Poly(acrylic acid) | 5,000 |
| Poly(acrylic acid) | 250,000 |
| Poly(vinyl sulfonate) sodium salt | 7,000 |
| Polystyrenesulfonate sodium salt | 70,000 |
| Poly(diallyldimethylammonium chloride) | 250,000 |
| Poly(4-vinylpyridine) | 50,000 |
| Polyvinylsulfate potassium salt | 350,000 |

The molecular sizes of the polyelectrolytes used also directly affect the number of depositions needed for a good membrane. The molecular size of a polyelectrolyte is directly related to the molecular weight of the polyelectrolyte. The polyelectrolytes used in the literature for making self-assembled double layers have relatively low molecular weights. Table 3-1 is a summary of the molecular weights of some polyelectrolytes used in the literature for making composite membranes with porous substrates.

The molecular size of a polymer can be estimated theoretically according to polymer chain statistics [He et al. 1990].

If all the carbon atoms in a polymer chain form a straight line, this polymer chain is defined as a fully extended polymer chain. The mean square end-to-end distance ($h^2$) of a fully extended polymer chain is

$$h^2 = n^2 l^2 \tag{3-1}$$

where $n$ is the number of C-C bonds in a polymer backbone and $l$ is the bond length.

If each bond in a polymer chain can rotate freely in the direction that is stipulated by the bond angle, the polymer chain is a freely rotating chain and the mean square end-to-end distance of a freely rotating chain ($\overline{h}_{f,r}^2$) is

$$\overline{h}_{f,r}^2 = nl^2 \frac{1+\cos\theta}{1-\cos\theta} \tag{3-2}$$

where $\theta$ is the complementary angle of bond angle.

The mean square end-to-end distance of an actual polymer chain is

$$\overline{h}_{actual}^2 = nl^2 \frac{1+\cos\theta}{1-\cos\theta} \frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} = \overline{h}_{f,r}^2 \frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \tag{3-3}$$

and $$\overline{\cos\phi} = \frac{\int_0^{2\pi} e^{-u(\phi)/kT} \cos\phi d\phi}{\int e^{-u(\phi)/kT} d\phi} \tag{3-4}$$

where $u(\phi)$ is the potential for internal bond rotation and $\phi$ is the internal rotation angle.

The radius of gyration ($r$) of a polymer can be obtained from the mean square end-to-end distance.

$$r^2 = \frac{h^2}{6} \tag{3-5}$$

It is therefore possible to calculate the mean square end-to-end distance and the radius of gyration of a polymer if we know the molecular weight (number of repeat units) and the chemical structure (bond angle and bond length) of a polymer.

Table 3-2 is the calculated mean square end-to-end distances and the radii of gyration of the polyelectrolytes used in the literature for making self-assembled composite membranes.

**Table 3-2. Calculation of the molecular sizes of polyelectrolytes used in the literature for making membranes**

| Polyelectrolyte | Fully Extended Chain | | Freely Rotating Chain | |
|---|---|---|---|---|
| | $h^2$(nm$^2$) | $r$ (nm) | $h^2$(nm$^2$) | $r$ (nm) |
| Poly(allylamine hydrochloride) | 1005 | 13 | 10 | 1.3 |
| Polyvinylamine | 512656 | 292 | 220 | 6.1 |
| Poly(acrylic acid) | 467 | 9 | 7 | 1.0 |
| Poly(acrylic acid) | 1142761 | 436 | 330 | 7.4 |
| Poly(vinyl sulfonate) sodium salt | 276 | 7 | 5 | 1.0 |
| Polystyrenesulfonate sodium salt | 11025 | 42.9 | 32 | 2.3 |
| Poly(diallyldimethylammonium chloride) | 910116 | 389 | 294 | 6.9 |
| Poly(4-vinylpyridine) | 21609 | 60 | 5 | 2.7 |
| Polyvinylsulfate potassium salt | 448900 | 274 | 12 | 5.8 |

The fully extended polymer chain is an extreme case. In fact, no polymer chain can be a fully extended chain because, at least, the bond angle prevents the formation of a fully extended polymer chain. The size of an actual polymer chain is always much smaller than the size of a fully extended chain with the same molecular weight. On the other hand, an actual polymer chain is more rigid than a freely rotating chain because the rotation around a C-C bond in an actual polymer chain is not totally free and the size of an actual polymer chain is thus larger than that of a freely rotating chain. Therefore the size of a real polymer chain in a deposition solution is always smaller than the size of its fully extended chain but larger than the size of its freely rotating chain.

According to Table 3-2, the molecular sizes of some polyelectrolytes used in the literature, even in fully extended conformation, are still about the same or smaller than the largest pore (200 nm) on the porous substrate used. The largest fully extended polyelectrolyte chain length is only 872 nm, which is 4.5 times the size of the largest pore on the porous substrate used. The actual size of a polyelectrolyte chain is much smaller than the size of a fully extended polymer chain with the same molecular weight because of coordinated and multiple rotation of chemical bonds in a polymer chain. It is quite possible that the largest molecular size in all the polyelectrolytes used in the literature (listed in Table 3-2) could be about 200 nm or smaller than 200 nm that is the size of the largest pores on the porous substrate. For the poly(allylamine hydrochloride) with molecular weight of 9,600, the fully extended chain length is less than 30 nm (much smaller than the largest pore on the porous substrate used), and therefore there is no doubt that this polyelectrolyte molecule will go into the pores if it is used for depositions. When the molecular size of a polyelectrolyte is smaller than 200 nm, it is impossible to use this polyelectrolyte chain to directly cover a pore with the size of 200 nm unless the pore size can be reduced in some way. It is clear that if the polyelectrolytes listed in Table 3-2 are used to make a composite membrane with a porous substrate having pore sizes as large as 200 nm, the polyelectrolytes will definitely go into the pores on the substrate. It appears that the molecular sizes of the polyelectrolytes used in the literature were too small while the pore size of the porous substrate used was too large. Both the selection of a porous substrate and the selection of polyelectrolytes in the literature for making composite self-assembled membranes seemed inappropriate.

Because the materials used in the literature for making self-assembled composite membranes were not appropriate, many of the self-assembly depositions on the porous substrate were filling depositions. If the number of these filling depositions can be reduced, the total number of depositions needed for making a self-assembled composite membrane will be reduced.

The number of filling depositions in making a self-assembled separating layer on a porous substrate can be reduced by reducing the pore size of the porous substrate and/or increasing the molecular sizes of the polyelectrolytes. Therefore, it is expected that the

number of double layers needed for making a self-assembled separating layer can be reduced in the same way.

This concept actually has already been proved by Meier-Haack et al. [2001] who used non-porous materials as substrates to make self-assembled composite membranes. It was reported that before electrostatic self-assembly depositions, the non-porous substrates had a separation factor lower than 10 for the dehydration of a mixture of IPA and water (70/30). After 8 deposition cycles with polyethylenimine and alginic acid solutions, the composite polyelectrolyte membrane had a separation factor over 10,000. This showed that a large number of self-assembled double layers were not always necessary to obtain a high separation factor. The thing is that a defect-free separating layer has to be formed over the supporting material. This implies that if the pore size of a porous substrate is small enough, the fabrication of self-assembled composite membranes on porous substrates will be similar to the fabrication of self-assembled composite membranes on a non-porous substrate. It is possible to make composite membranes with reduced self-assembled double layers if appropriate materials are selected.

Either reducing the pore size of a porous substrate or increasing the molecular sizes of the polyelectrolytes, theoretically, can reduce the number of depositions required to cover all the pores on the porous substrate. In this work, reducing the pore size of a porous substrate and increasing the molecular sizes of polyelectrolytes were used at the same time and the number of self-assembled double layers needed for covering all the pores on the porous substrate was expected to be substantially reduced. The objective of this chapter was to confirm the possibility of making composite polyelectrolyte pervaporation membranes with less than 10 self-assembled double layers and with good dehydration performance by using an appropriate substrate and appropriate polyelectrolytes.

# 3.2 Experimental

## 3.2.1 Materials

PAN ultrafiltration membranes with nominal molecular weight cut-off (MWCO) 20,000 and 30,000 were used as original porous supporting materials for the fabrication of composite membranes. The PAN ultrafiltration membranes used consisted of a porous PAN layer and a polyester backing layer.

Polyethylenimine (50 wt% solution in water, Mw 750, 000), chitosan powder (Mw 600,000), poly(acrylic acid) (35wt% solution in water, Mw 250,000) and poly(diallyldimethylammonium chloride) (20 wt% solution in water, Mw 200,000-350,000) were all from Aldrich. Polyethylenimine used here has a short branched structure. Both polyethylenimine and chitosan were used as polycations. Poly(acrylic acid) powder (Mw 1,000,000) provided by Polysciences was also used.

Sodium hydroxide (GR) from Merck KGaA, Damstadt, Germany, IPA from EM Science, Merck KGaA, Damstadt, Germany, and hydrochloric acid (37 wt% solution in water) from Aldrich were used in the experiment.

De-ionized water was used as the solvent to make polyelectrolyte deposition solutions.

## 3.2.2 Hydrolysis of the porous PAN membranes

To obtain a charged porous substrate for making a self-assembled composite membrane, a porous PAN membrane was hydrolyzed first. After being washed with de-ionized water, the surface of the hydrolyzed PAN membrane was negatively charged.

The hydrolysis was carried out as follows. A container with 1N solution of sodium hydroxide was heated to a predetermined temperature in a controlled water bath

and then porous PAN membranes were immersed into this solution for a given period of time. After thorough washing with de-ionized water, hydrolyzed PAN membranes were obtained. The contact angles of resulting hydrolyzed porous PAN membranes were measured to monitor the hydrolysis of the PAN membranes using a Tantec cam-plus series of contact angle meter.

### 3.2.3 The Pore size of the porous PAN substrate membranes

The pore size of a PAN substrate membrane in the dry state is different from that in the wet state. The mean pore size of a porous PAN membrane in the dry state was determined with a gas permeation test using nitrogen as the permeating gas.

Generally, the gas permeance, B, of a porous material can be expressed as a function of both the diffusive term and the convective term that depends on the pressure [Khayet et al. 2002, 2003]:

$$B = \frac{4}{3}\left(\frac{2}{\pi MRT}\right)^{0.5}\frac{r_p\varepsilon}{L_p} + \frac{P_m}{8\mu RT}\frac{r_p^2\varepsilon}{L_p} = I_0 + S_0 P_m \qquad (3\text{-}6)$$

where R is the gas constant, T the absolute temperature, M the molecular weight of the permeating gas, $\mu$ the gas viscosity, $P_m$ the mean pressure within the membrane pore, $r_p$ the membrane pore radius, $\varepsilon$ the porosity, and $L_p$ the effective pore length.

From the intercept ($I_0$) and the slope ($S_0$) of a linear relation between permeance (B) and the mean pressure ($P_m$), the mean pore radius of a porous material can be calculated using the following formula [Khayet et al.2002,2003]:

$$r_p = \frac{16}{3}\left(\frac{S_0}{I_0}\right)\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \qquad (3\text{-}7)$$

This method was originally developed for the characterization of symmetric membranes. For asymmetric membranes, the measured pore size is considered as the characteristic of the skin layer. The pore size of a porous material determined in a gas permeation test is the pore size in the dry state.

The relative pore size of the porous PAN membranes in the wet state was determined by pure water permeation measurements. A Millipore cell (Swinnex-47) and a Masterflex pump were used for pure water permeation measurements. The diameter of the membrane sample used in the experiment was 4.3 cm. Three samples were used for each pure water permeation test and each sample was tested twice. The average of these six pure water permeation measurements was considered as the pure water permeation of the membrane sample at given test conditions. The test pressure was 10 psig and the test temperature was 25$^{O}$C.

### 3.2.4 Preparation of self-assembled composite membranes

The hydrolyzed porous PAN membrane, which was negatively charged, was first thoroughly washed with de-ionized water, and then polycations and polyanions were alternatively deposited on the hydrolyzed porous PAN membrane. Excessive polyions on the surface of the self-assembled layers were washed away by de-ionized water prior to subsequent deposition of oppositely charged polyelectrolyte. The deposition of individual polyelectrolyte layers was accomplished by immersing the base membrane into the polyelectrolyte solution. The basic steps involved in the self-assembling of the layer-by-layer structure consisted of: i) immersing the support membrane in the solution of a cationic polyelectrolyte for the initial disposition of polycations, ii) immersing in de-ionized water to wash the excessive polycations, iii) immersing in the solution of an anionic polyelectrolyte, and iv) immersing in de-ionized water again to wash excessive polyanions. As such, a pair of the self-assembled polyelectrolyte layers was formed. These steps were repeated as many times as necessary to form a polyelectrolyte multilayer by depositing polycations and polyanions alternatively.

The self-assembly deposition on a porous substrate can be conducted in two different ways: two-sided deposition and one-sided deposition. Simply dip a hydrolyzed porous PAN membrane into a polycation deposition solution, the electrostatic self-assembly deposition will take place on both sides of the hydrolyzed porous PAN membrane. This is a two-sided deposition method, and this is the deposition method extensively used in the literature to make composite membranes. In addition to two-sided deposition, one-sided deposition was also investigated in this work. One-sided deposition, as the name implies, is a process in which deposition only applies on the one side of the substrate. A bottle deposition technique was used to do one-sided depositions in this work. The hydrolyzed porous PAN substrate membrane is mounted in a sealing cap assembly of a wide-mouth bottle so that the PAN side of the substrate membrane faced the contents of the bottle. Then, place the polyelectrolyte solution to be deposited in the bottle, seal the bottle with the cap assembly and set the bottle upside down. In this way, the polyelectrolyte deposition solution would only contact the PAN side of the hydrolyzed PAN membrane. Preferably, the same cap assembly fit all three bottles containing respectively the anionic and cationic polyelectrolyte solutions (for polyelectrolyte deposition) and de-ionized water (for removal of excessive polyions) to facilitate the deposition operations. Both two-sided deposition and one-sided deposition methods were used at the beginning to make self-assembled composite membranes. After the comparison of the separation performance of the membranes made with these two methods, the one-sided deposition method was selected for further studies.

According to the movement of deposition solutions, self-assembly depositions can be classified into two categories. If the deposition solution moves constantly in a deposition process, this deposition is a dynamic deposition. If the deposition solution does not more in a deposition process, this deposition is a static deposition. In order to make a dynamic deposition, a special unit is needed to constantly rotate or shake the deposition solution. In contrast, a static deposition is very simple. Just let the deposition solution contact the surface to be deposited for some time and a static deposition will take place. Therefore, a static deposition was used throughout this work unless it was specified elsewhere.

Polyelectrolyte solutions with concentration of 0.02 monomol/L (monomol= mole of monomer unit) and 0.2 monomol/L were used in this work. Both fresh deposition solutions and reused solutions were used. A fresh deposition solution is a solution that has not been used for any depositions, while a reused deposition solution is a solution that has been used for the fabrication of a self-assembled membrane. Fresh or reused solution is only referred to the solution that is used for the deposition of the first double-layer on a hydrolyzed PAN membrane. When a solution has been used for the deposition of the first double-layer of a membrane, the same solution will be used for the depositions of the other double-layers in the same self-assembled membrane.

After multiple depositions, the membrane obtained needs to be treated under certain temperature for some time. This process is called post-treatment. Post-treatment temperature was selected between room temperature and $85^{O}C$ that is the Tg of PAN. Post-treatment time was several hours.

### 3.2.5 Pervaporation

A typical pervaporation testing unit, shown in Figure 3-1, was used to test the separation performance of the composite polyelectrolyte pervaporation membranes. It consisted of a feed tank, a feed temperature control unit, a feed circulation pump, a membrane testing cell, two cold traps and a vacuum pump. Feed temperature was controlled with a water bath. The liquid feed, after being heated to a pre-determined temperature, was pumped to flow over the active surface of a composite membrane and the residue stream was recycled back to the feed tank. The effective area of the membrane in the membrane testing cell was 13.9 $cm^2$. Figure 3-2 shows the testing cell used. The feed circulation rate was kept sufficiently high to minimize the boundary layer effect on the membrane productivity. Vacuum was applied to the permeate side of the membrane, and the permeate pressure was maintained below 5 mmHg absolute. The permeate vapor was condensed and collected in a Pyrex glass cold trap immersed in liquid nitrogen. The permeation rate was determined gravimetrically by weighing the permeate sample collected over a given period of time, and the compositions of the feed

and permeate streams were analyzed using a Hewlett Packard 5890 gas chromatography. In order to minimize the variation in the feed composition during a pervaporation run, the quantity of permeate removed by the membrane during the run was maintained below 0.1% of the initial feed loaded in the feed tank. This work is concerned with steady state pervaporation. A steady state of pervaporation is considered to have been reached when both the permeation rate and permeate composition become constant. The membrane performance was characterized in terms of permeation flux and separation selectivity. The overall permeation flux was determined using Eqn. (2-1) and the selectivity can be determined using Eqn. (2-2). In this work, the selectivity of the membrane was expressed by the water concentration in permeate because the feed compositions were almost constant. IPA/water mixtures were used as feed in the experiments and the water concentration in feed was in the range of 8-9 wt% during the pervaporation experiments except when specified otherwise.

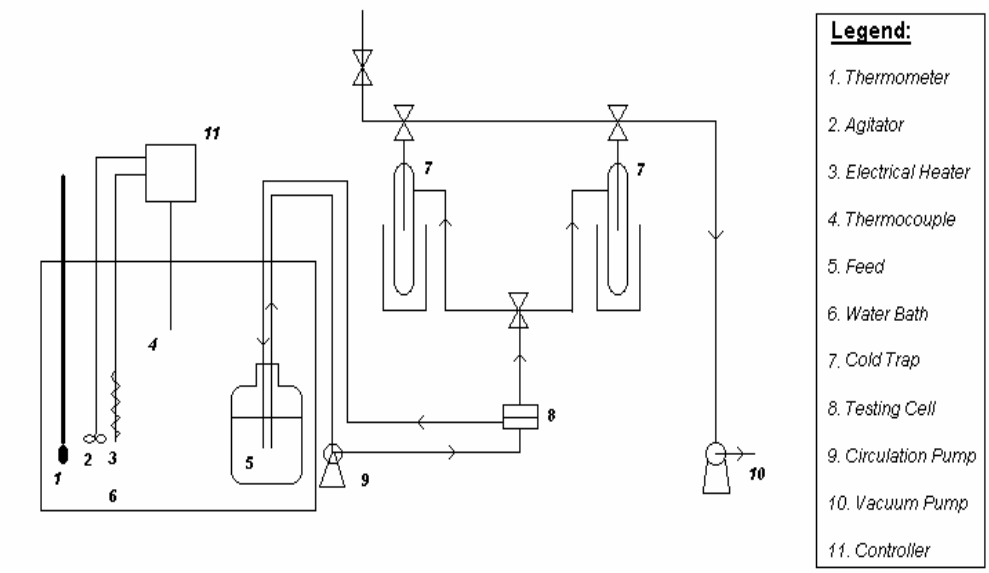



**Figure 3-1. Pervaporation testing unit**

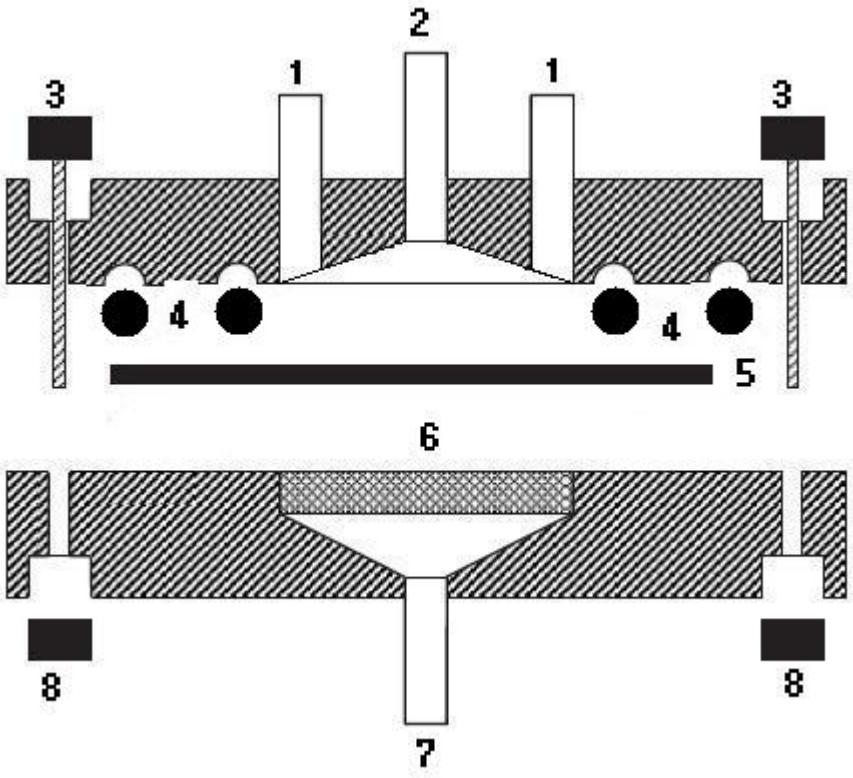



**Figure 3-2. Pervaporation testing cell**

1. Retentate outlet 2. Feed inlet 3. Bolt 4. O-ring 5. Membrane
6. Sintered stainless steel plate 7. Permeate pipe 8. Nut

# 3.3 Results and discussion

## 3.3.1 Selection of a porous substrate

In order to use the electrostatic self-assembly technique, the surface of the substrate needs to be charged. There are two ways to make a charged surface. One is to incorporate a charged polymer (or charged polymers) into the formulation of the porous

substrate, another one is to modify the surface of an un-charged porous substrate to make it charged. Blending a charged polymer into the composition of a porous substrate is relatively complicated because a charged polymer in the composition of a porous material can change the conditions of making a porous substrate. Also blending a charged polymer into the composition of a porous substrate can affect the chemical resistance, thermal resistance and mechanical strength of the porous substrate obtained. From this point of view, surface modification of an un-charged substrate is an effective and simple way to obtain a charged surface.

A surface modification can be a physical or chemical modification. Only the surface properties of a substrate will be changed during a surface modification, and the chemical resistance, thermal resistance and mechanical strength of the substrate are not significantly affected. This is the advantage of using surface modification. Plasma treatment is a commonly used physical modification. Oxygen plasma treatment has been used in the literature to make an un-charged PAN surface negatively charged for the fabrication of a composite polyelectrolyte membrane. The charged surface obtained from a plasma treatment is not permanent. As time passes, the charges on the surface of modified substrate can disappear and the charged surface can become un-charged again. On the other hand, a charged surface obtained by chemical modification is permanent and the surface charges will remain all the time. In this work, a chemical surface modification method was used to make the charged supporting material.

There are different kinds of porous membranes that can be used as porous substrates for making composite membranes, including ultrafiltration membranes made from polysulfone, polyethersulfone, poly(vinylidene fluoride) and PAN. Among these membranes, PAN membranes can be easily modified with a chemical reaction. By hydrolyzing a porous PAN membrane in an alkaline (sodium hydroxide) solution, the -CN groups on the surface of the PAN membrane will be transformed into carboxylic groups. The hydrolysis of PAN has already been studied, and the hydrolysis of PAN hollow fiber membranes has also been reported [Yang and Tong, 1997]. Hydrolyzing a porous PAN membrane is a convenient way to make a charged substrate for self-assembly depositions.

The pore size of a porous PAN membrane is very important in selecting an appropriate porous substrate. The pore size of the substrate needs to be small enough to reduce the number of depositions needed to cover all the pores on the porous substrate, however if the pore size is too small, the material transport resistance through the supporting layer of the composite membrane will be high, leading to a low permeation flux. Therefore the pore size of a porous PAN membrane needs to be in an optimal range.

A porous commercial PAN membrane with a nominal MWCO of 20,000 was first selected as a base material for supporting layer in this work. The pore size of the porous PAN membrane was experimentally determined. Table 3-3 shows the gas permeation rate of three un-hydrolyzed PAN membrane samples at $25^{O}C$.

**Table 3-3. Gas permeation rate of un-hydrolyzed porous PAN membranes**

| Feed gas pressure (kPa) | Gas permeance ($m^3/m^2sPa$)$\times 10^8$ | | |
|---|---|---|---|
| | Sample 1 | Sample 2 | Sample 3 |
| 34.5 | 1.08 | 1.06 | 1.05 |
| 69.0 | 1.12 | 1.11 | 1.11 |
| 103.4 | 1.25 | 1.25 | 1.24 |
| 137.9 | 1.34 | 1.34 | 1.34 |

Permeate gas pressure= 101.3 kPa

Figure 3-3 shows the relation between the permeance of un-hydrolyzed porous PAN membranes and the feed gas pressure.

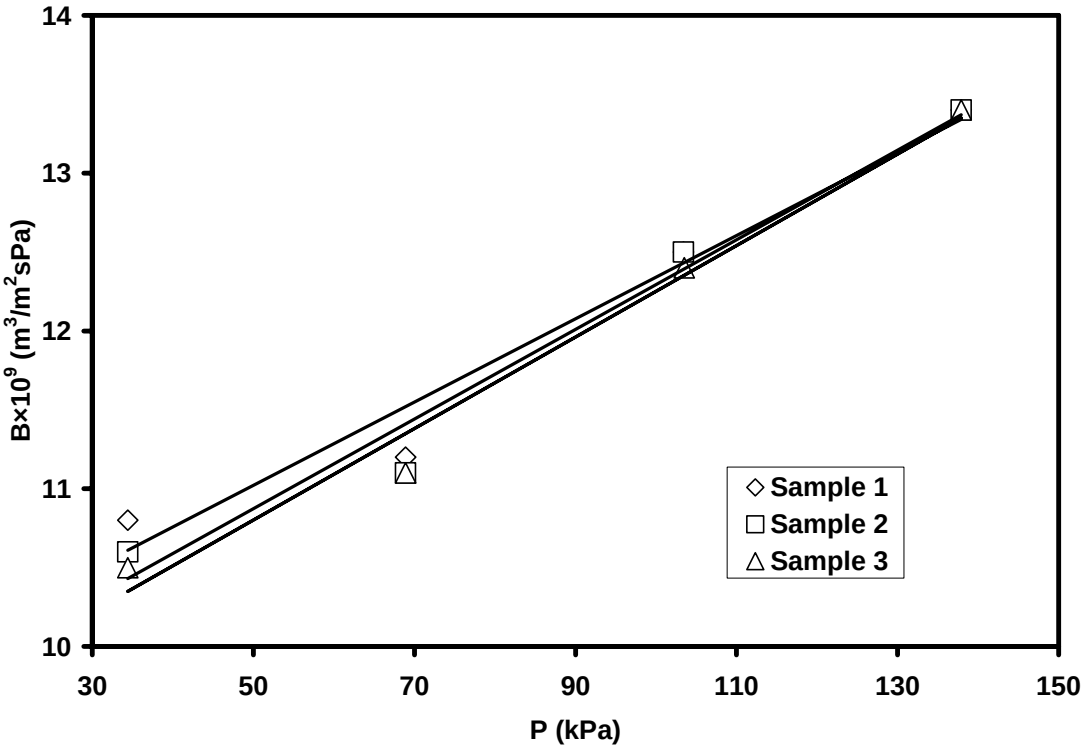



**Figure 3-3. Gas permeance and pressure of un-hydrolyzed PAN membranes**

Table 3-4 is the linear fitting data of the gas permeation experiments of three un-hydrolyzed porous PAN membranes with nominal MWCO of 20,000. The pore sizes of the un-hydrolyzed PAN membranes, calculated by using Equation 3-7, are also given in Table 3-4.

**Table 3-4. Linear fitting data of gas permeation experiment of un-hydrolyzed porous PAN membranes**

| Un-hydrolyzed Membrane | Slope $S_o \times 10^{14}$ ($m^3/m^2s$) | Intercept $I_o \times 10^9$ ($m^3/m^2sPa$) | Pore Radius (nm) |
|---|---|---|---|
| Sample 1 | 2.63 | 9.67 | 3.9 |
| Sample 2 | 2.80 | 9.49 | 4.2 |
| Sample 3 | 2.83 | 9.43 | 4.3 |

These permeation data show that the un-hydrolyzed porous PAN membranes used in this work had very fine pores. The average pore diameter was below 10 nm, and this agrees with the literature data. According to the "filtration spectrum" published by Osmonics, the molecular size of a saccharide with molecular weight of 20,000 is about 10 nm. The actual pore size of an ultrafiltration membrane with a MWCO of 20,000 should be little smaller than 10 nm to prevent the passing of the saccharide with molecular weight of 20,000. The average pore size of the un-hydrolyzed porous PAN membranes used in this study was roughly 8.2 nm, which was indeed smaller than 10 nm.

To obtain a charged porous substrate for making a self-assembled separating layer, the un-hydrolyzed porous PAN membrane needed to be hydrolyzed first. The hydrolysis conditions affect the pore size and the surface charge density of the hydrolyzed porous PAN membrane. When the hydrolysis temperature is increased or the hydrolysis time is prolonged, more surface –CN groups will be transformed into carboxyl groups, and as such, the surface contact angle will be decreased. By monitoring the change of contact angles of the porous PAN membrane, the hydrolysis process can be monitored. Tables 3-5 and 3-6 show the effects of hydrolysis times and hydrolysis temperatures on the contact angles of hydrolyzed PAN membranes.

**Table 3-5. Effect of hydrolysis times on the contact angles of porous PAN membranes (hydrolysis temperature 75$^{O}$C)**

| Hydrolysis time (min) | 30 | 20 | 10 | 0 |
|---|---|---|---|---|
| Contact angle ($^{O}$) | 60 | 68 | 72 | 86 |

**Table 3-6. Effect of hydrolysis temperatures on the contact angles of porous PAN membranes (hydrolysis time 20 min)**

| Hydrolysis temperature ($^{O}$C) | 80 | 75 | 70 | 0 |
|---|---|---|---|---|
| Contact angle ($^{O}$) | 38 | 68 | 80 | 86 |

Hydrolysis can happen on the PAN layer, the polyester supporting side and at the interface between these two layers in a porous PAN membrane. Ideally, hydrolysis should only happen on the active surface of the PAN side to maintain the mechanical strength of hydrolyzed product. But it is very difficult to do so. The only way to maintain the mechanical strength of the hydrolyzed PAN membrane is to control the degree of hydrolysis. When most of the surface –CN groups have been converted into carboxylic groups, further hydrolysis will not increase the number of carboxylic groups on the surface but will reduce the mechanical strength of the hydrolyzed PAN membrane. Thus the hydrolysis should be stopped when the contact angles of the hydrolyzed porous PAN membrane become constant.

The hydrolysis changes not only the surface contact angle of a porous PAN membrane, but also the pore size of the membrane. The pore size of a hydrolyzed porous PAN membrane is different from that of an un-hydrolyzed one. The pore size of a hydrolyzed porous PAN membrane directly affects the number of self-assembled double layers needed for making a defect-free self-assembled composite membrane and the performance of the resulting composite membrane. The pore sizes of the hydrolyzed porous PAN membranes were also determined by the gas permeation technique. It was found that the gas flow rates through all hydrolyzed porous PAN membranes were several times higher than that through the un-hydrolyzed porous PAN membrane. Table 3-7 is the gas permeation rate of a typical hydrolyzed porous PAN membrane. It can be found from Tables 3-7 and 3-3 that the nitrogen permeation rate of a typical hydrolyzed porous PAN membrane was roughly 30 times higher than that of un-hydrolyzed porous PAN membranes under the same experimental conditions. This means that the pore sizes of hydrolyzed PAN membranes in the dry state were larger than that of the un-hydrolyzed porous PAN membranes. Because the gas flow rates were too high to be precisely measured under the experimental conditions, the pure water permeation experiments were used to measure the relative pore size of the hydrolyzed and un-hydrolyzed porous PAN membranes in the wet state. Table 3-8 contains pure water permeation data of hydrolyzed and un-hydrolyzed porous PAN membranes.

For all self-assembled depositions, the pore size of a porous substrate in the wet state is more important than that in the dry state because actual depositions are always carried out in the wet state.

**Table 3-7. Gas permeation data of a typical hydrolyzed porous PAN membrane**

| Feed gas pressure (kPa) | Gas permeation rate $\times 10^7$ ($m^3/m^2sPa$) |
|---|---|
| 17.2 | 3.01 |
| 34.5 | 3.05 |
| 51.7 | 3.24 |
| 68.9 | 3.35 |

Hydrolysis temperature: 75$^{O}$C  Hydrolysis time: 20 min.

**Table 3-8. Pure water permeation rate of porous PAN membranes**

| Hydrolysis conditions | | Pure water permeation rate ($kg/m^2hr$ @ 10 psig) |
|---|---|---|
| Temperature ($^{o}$C) | Time (min) | |
| Un-hydrolyzed | Un-hydrolyzed | 57.5 |
| 70 | 20 | 166 |
| 75 | 10 | 85.8 |
| 75 | 20 | 31.5 |
| 75 | 30 | 20.0 |
| 80 | 20 | 20.4 |

The data in Table 3-8 show that the pure water permeation rate of an un-hydrolyzed porous PAN membrane was different from that of a hydrolyzed one, which

indicates that the hydrolysis did change the pore size of the porous PAN membrane in the wet state. The pure water permeation rate of a hydrolyzed porous PAN membrane changed as hydrolysis conditions changed. The general trend is that, compared with an un-hydrolyzed porous PAN membrane, the pure water permeation rate of a hydrolyzed PAN membrane initially increased either at a low hydrolysis temperature ($70^{O}C$) or in a short hydrolysis period of time (10 min) and then decreased. It is difficult to explain why the pure water permeation rate increased when the degree of hydrolysis was low, but it is easy to explain why the pure water permeation rate decreased when the degree of hydrolysis was a little higher. As the hydrolysis time increased or the hydrolysis temperature increased, the degree of hydrolysis increased and more –CN groups were converted into carboxylic groups on the surface of the porous PAN membrane and on the inner surface of the pores. These carboxylic groups could form a highly swollen and highly hydrophilic layer on the inner surface of the pores, which would increase the resistance for water to go through the pores and would reduce the pure water permeation rate of the hydrolyzed membrane. The pure water permeation rate of a PAN membrane hydrolyzed at $70^{O}C$ for 20 min was significantly higher than that of other hydrolyzed PAN membranes and even higher than that of an un-hydrolyzed PAN membrane because the swelling of small amount of carboxylic groups on the surface of hydrolyzed PAN membrane (pore size reduction) could not compensate the increase in pore size in hydrolysis. As the degree of hydrolysis increased, the swelling of surface carboxylic groups increased rapidly and hydrolyzed PAN membranes would have reduced pore size in the wet state.

From the pure water permeation rate, it was found that when a PAN membrane was hydrolyzed at $75^{O}C$ for 20 min, the pore size of the hydrolyzed porous PAN membrane in the wet state was smaller than that of the un-hydrolyzed porous PAN membrane. The pore size of the substrate in the wet state did not increase after hydrolysis and it is therefore possible to use a porous PAN membrane with a nominal MWCO of 20,000 to make a self-assembled composite membrane.

Based on considerations of mechanical stability and separation performance of the composite membrane obtained, porous PAN membranes with a MWCO of 20,000 were

hydrolyzed at 75$^{O}$C for 20 min to become negatively charged, and the charged porous substrates were used for self-assembly depositions.

Plasma-treated porous PAN membranes have been used as porous substrates for the fabrication of composite membranes and there are several reports in the literature about the use of plasma-treated porous PAN membranes. Table 3-9 gives a summary of polyelectrolytes and deposition conditions used in the literature for making composite membranes using plasma-treated porous PAN membranes as porous substrates. To our knowledge, there has not been any report on using hydrolyzed porous PAN membranes as porous substrates to make self-assembled composite membranes. This is the first time that hydrolyzed porous PAN membranes are used as porous substrates to make composite membranes.

In order to see if a hydrolyzed porous PAN membrane is a good porous substrate for making a composite membrane, an un-hydrolyzed porous PAN membrane and a hydrolyzed porous PAN membrane (hydrolyzed at 75$^{O}$C for 20 min) were used as substrates to make two self-assembled membranes and the separation performance of the membranes were compared with each other.

To prepare the composite membrane, the porous PAN substrate (hydrolyzed or un-hydrolyzed) was dipped into a 0.02 monomol/L polyethylenimine solution and a 0.02 monomol/L poly(acrylic acid) solution alternatively, and between the two depositions the deposited layer was washed three times in de-ionized water. After 16 depositions (i.e. 8 deposition cycles), the dehydration performance of the membrane was tested with an aqueous IPA solution that contained 11 wt% of water.

The flux of the membrane made with an un-hydrolyzed porous PAN membrane as the substrate was higher than 2.8 kg/m$^2$hr and the water concentration in permeate was about 18 wt%. Obviously the separation performance of the membrane made with an un-hydrolyzed substrate was rather poor. In contrast, the separation performance of the membrane made with a hydrolyzed porous PAN membrane as the substrate was much better, as shown in Table 3-10.

**Table 3-9. Plasma-treated porous PAN membrane used as substrates for making composite polyelectrolyte pervaporation membranes in the literature**

| Substrate (pore size) | Polyelectrolytes | Conc. of deposition solution(monomol/l) | No. of cycles | Ref. |
|---|---|---|---|---|
| PAN/PET [a] (20-200 nm) | Polyvinylamine ($M_w$ 100,000)<br>Poly(allylamine hydrochloride) ($M_w$ 9,600)<br>Poly(styrene sulfonate sodium salt) ($M_w$ 70,000)<br>Polyethylenimine ($M_w$ 70,000)<br>Chitosan ($M_w$ 100,000)<br>Poly(diallyldimethyl ammonium chloride) ($M_w$ 250,000) | 0.01 | 60 | Toutianoush, Krasemann & Tieke (2002) |
| PAN /PET (20-200nm) | Poly(allylamine hydrochloride)<br>Poly(styrene sulfonate sodium salt )<br>1.4-diketo-3.6-diphenylpyrrolo-[3,4-c]-pyrrole-4.4-disulfonic acid<br>10.22-docosadiyne-1.22-disulfate disodium salt | 0.0002-0.01 | 60 | Arkern, Krasemann & Tieke (1998) |
| PAN/PET (20-200nm) | Poly(allylamine hydrochloride) ($M_w$ 9,600)<br>Poly(styrene sulfonate sodium salt) ($M_w$ 70,000) | 0.01 | 30-90 | Krasemann & Tieke (1998) |
| PAN /PET (20-200nm) | Poly(allylamine hydrochloride) ($M_w$ 9,600)<br>Poly(styrene sulfonate sodium salt )($M_w$ 70,000)<br>Chitosan ($M_w$ 100,000)<br>Poly(vinyl pyridine) ($M_w$ 50,000)<br>Polyethylenimine ($M_w$ 70,000)<br>Dextran sulfate ($M_w$ 5,000)<br>Polyvinylamine ($M_w$ 100,000)<br>Poly(vinyl sulfate potassium salt) ($M_w$ 350,000) | 0.01 | 60 | Krasemann, Toutianouch & Tieke (2001) |
| PAN /PET (20-200nm) | Polyvinylamine ($M_w$ 100,000) | 0.01 | 60 | Tieke et al. (2001) |

| | | | | |
|---|---|---|---|---|
| | Poly(vinyl sulfate potassium salt) ($M_w$ 350,000) | | | |
| PAN /PET (20-200nm) | Polyvinylamine ($M_w$ 100,000)<br>Poly(vinylsulfate potassium salt) ($M_w$ 350,000) | 0.01 | 60 | Toutianouch & Tieke (2002-2) |
| PAN /PET (20-200nm) | Poly(allylamine hydrochloride)<br>Polyethylenimine<br>Polyvinylamine<br>Chitosan<br>Poly(diallyldimethyl ammonium chloride)<br>Poly(4-vinylpyridine)<br>Poly(styrenesulfonic acid)<br>Poly(vinylsulfate potassium salt)<br>Dextransulfate sodium salt<br>1.4-diketo-3.6-diphenylpyrrolo-[3,4-c]-pyrrole-4.4-disulfonic acid | | 60 | Tieke et al. (2001) |

[a] PET=polyethyleneterephthalate

**Table 3-10. Pervaporation performance of a composite membrane made with a hydrolyzed porous PAN membrane as porous substrate**

| No. of deposition cycles[a.b] | Temp. ( $^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate[c] (wt%) |
|---|---|---|---|
| 8 | 50 | 0.65 | 89.3 |
| 8 | 60 | 0.81 | 96.4 |

[a] two-sided depositions

[b] polyelectrolytes: poly(acrylic acid), Mw250,000; polyethylenimine Mw750,000 the porous PAN membrane was hydrolyzed at 75$^{O}$C for 20 min.

[c] water concentration in feed was 11.0 wt%

From the separation performance of these two membranes, it is clear that by using a hydrolyzed porous PAN membrane as a substrate, the composite membrane obtained had a lower flux but much better separation selectivity. The possible reason for this is as follows. When a hydrolyzed porous PAN membrane was used as a substrate, there were negative charges on the surface of the porous substrate and these charges would interact with the charges on the cationic polyelectrolyte chains in the deposition solution in a deposition process. Cationic polyelectrolytes would be adsorbed onto the charged surface of the porous substrate via electrostatic forces. The amount of cationic polyelectrolyte adsorbed onto the surface depended on the charge density on the surface of the substrate and the polyelectrolyte concentration in the deposition solution. When an un-hydrolyzed porous PAN membrane was used as a substrate, only a very small amount of polyelectrolyte could be adsorbed onto the un-charged surface of the porous substrate via van der Waals forces. As a result, the thickness of the deposited polyelectrolyte layer on an un-hydrolyzed porous PAN membrane was much smaller than that on a hydrolyzed porous PAN membrane. The thinner the separating layer, the lower the selectivity. It

appears that hydrolyzed porous PAN membranes are good porous substrates for making self-assembled composite membranes.

## 3.3.2 Selection of polyelectrolytes

Different polyelectrolytes have different characteristics, e.g. charge density, structure (linear or branched), and electrolyte type (weak or strong). First, we need to select suitable types of polyelectrolytes because it has been noticed that the dehydration performance of some polyelectrolyte pairs is always poor no matter how thick the polyelectrolyte complex layer is. For a high performance composite membrane, the separating layer should be very thin and very selective. Poly(acrylic acid) and polyethylenimine were pre-selected in this work because this polyelectrolyte pair had good separation performance for the dehydration of IPA/water mixtures [Meier-Haack et al. 2001]. As a comparison, poly(diallyldimethylammonium chloride), a strong polycation with low charge density, and chitosan, a weak polycation with low charge density, were also used to study the effect of the type of polyelectrolyte on the separation performance of the composite membranes obtained. Table 3-11 gives the molecular weights of the polyelectrolytes used in this work.

**Table 3-11. Molecular weights of polyelectrolytes used in this work**

| Polyelectrolytes | Molecular weight |
|---|---|
| Poly(acrylic acid) | 250,000<br>1,000,000 |
| Polyethylenimine | 750,000 |
| Poly(diallyldimethylammonium chloride) | 200,000-300,000 |
| Chitosan | 600,000 |

Compared with the molecular weights of polyelectrolytes listed in Table 3-1, the molecular weights of the polyelectrolytes used in this work were much higher than those used in the literature for making composite membranes. In addition to the type of polyelectrolyte, the molecular size of a polyelectrolyte used for depositions is critical. The molecular size of a polyelectrolyte in a dilute deposition solution is mainly determined by its molecular weight. To prevent polyelectrolytes from going into the pores on a porous substrate, the molecular sizes of the polyelectrolytes should be much larger than the pore size of the porous substrate used. For this purpose, the molecular sizes of polyelectrolytes in dilute deposition solutions need to be estimated.

The unperturbed root-mean square end-to-end distance of poly(acrylic acid) in a dilute solution can be estimated with the following formula [Brandrup & Immergut, 1989]:

$$\frac{h_0}{M^{\frac{1}{2}}} = 756 \times 10^{-4} \text{ (nm)} \qquad (3\text{-}8)$$

where $h_o$ is the unperturbed root-mean square end-to-end distance (nm) and M the molecular weight of poly(acrylic acid).

Based on equation (3-8), the unperturbed root-mean square end-to-end distances for poly(acrylic acid) with $M_w$ 250,000 and 1,000,000 are 37.8 and 75.6 nm, respectively, that correspond to radii of gyration of 15.4 and 30.8 nm, respectively. These radii of gyration are unperturbed dimensions and the actual radii of gyration of the poly(acrylic acid) in water should be larger than unperturbed data because water is a good solvent for poly(acrylic acid) and the expansion factor of poly(acrylic acid) in water is larger than 1. But even when the expansion of poly(acrylic acid) in water is not taken into consideration, the unperturbed molecular sizes of the poly(acrylic acid) used in this work are still several times larger than the average pore size of the porous substrate used. In this case, these poly(acrylic acid) molecules have relatively small chances to go into the pores on the porous substrate.

Hellweg et al. [2000] used dynamic light-scattering to measure the size of a polyethylenimine sample with an average molecular weight of 25,000. They found that the radius of the polyethylenimine coil was about 4.6 nm at a pH of 7.4. The molecular weight of the polyethylenimine used in this work was 750,000 that was 30 times higher than the molecular weight of the polyethylenimine used by Hellweg et al., and the pH of the polyethylenimine deposition solution in this work was adjusted to about 5 to further increase the degree of ionization of the polyethylenimine used and the coil size of the polyethylenimine in solution. Therefore the average size of polyethylenimine coils in the deposition solution would be, qualitatively, larger than the pore size of the hydrolyzed porous PAN substrate and most of the polyethylenimine molecules would form deposition layers over the pores.

### 3.3.3 Selection of deposition method

Though a two-sided deposition method is simple and widely used for self-assembly deposition in the literature, it was found that if a membrane was made with a two-sided deposition method, there were some problems with the membrane obtained. Firstly, the structure and the thickness of a membrane made with a two-sided deposition method could not be controlled. Whenever a hydrolyzed porous PAN membrane was dipped into a suitable polyelectrolyte solution, depositions on the backside happened. However, the thickness of the deposition layer on the backside could be quite different at different points. Also the pore size on the backside was much larger than that on the PAN side. The depositions on the backside usually do not improve the selectivity of the membrane much but reduce the flux of the membrane significantly. Take the membrane mentioned in Table 3-10 as an example; since the membrane was made with the two-sided deposition method, the membrane obtained with 16 two-sided depositions had 32 polyelectrolyte layers. Yet the separation performance of this membrane was still not good. The reproducibility of the separation performance of a membrane made with the two-sided deposition method was rather poor. The relative error in fluxes among three membrane samples made under the same conditions was higher than 30%. The reason for

the poor reproducibility of a membrane made with a two-sided deposition method was that the depositions on the backside of a hydrolyzed porous PAN membrane were out of control.

Secondly, after two-sided depositions, the backside of a composite membrane was sticky and brittle. When this membrane was used for pervaporation experiments, the backside of the composite membrane was always stuck to the O-ring in the testing cell, and membrane delamination always happened when the membrane was taken out from the pervaporation testing cell. Also, the dried membrane sample made with two-sided depositions was easy to break. The self-assembled membranes made with two-sided depositions could hardly be used for practical applications.

There are two possible ways that the polyelectrolytes can reach the backside of a hydrolyzed porous PAN membrane. One way is to go through the pores on a hydrolyzed porous PAN membrane, and the other way is to go over the edges of a hydrolyzed porous PAN membrane. With suitably selected materials (i.e., a substrate with a relatively small pore size and polyelectrolytes with relatively high molecular weights), most polyelectrolytes will not pass through the pores on a porous substrate. Going over the edges of a hydrolyzed porous PAN membrane is the only pathway for the polyelectrolytes in deposition solutions to contact the backside of the substrate. If the polyelectrolytes in deposition solutions cannot contact the backside of a hydrolyzed porous PAN membrane by going over the edges of the substrate, the deposition of a polyelectrolyte on a porous PAN substrate will occur on the PAN side only. This is the principle of single-sided deposition (or one-sided deposition).

To prevent the polyelectrolytes from going over the edges of the porous PAN substrate, the bottle deposition technique was used in this work. Table 3-12 is the separation performance of a composite membrane having 10 double layers made with the one-sided deposition method. The depositions were conducted at room temperature.

**Table 3-12. Separation performance of a composite membrane made with one-sided deposition method**

| No. of deposition cycles | Temp. ( $^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt %) |
|---|---|---|---|
| 10 | 50 | 0.53 | 82.0 |
| 10 | 60 | 0.73 | 82.5 |

The separation performance of the membranes made with one-sided deposition was more reproducible than that of the membranes made with two-sided deposition which could have relative error more than 80% for between single samples. Because the membranes made with one-sided deposition had better consistency in performance and better mechanical strength, the one-sided deposition method was preferred for making self-assembled composite membranes.

A concentration-changing technique was developed in this work to reduce the number of depositions needed for making separating layers for composite membranes. The basic concept of this technique is easy to understand. When a polyelectrolyte deposition solution is dilute, each polyelectrolyte molecule forms one isolated coil. There is no interaction between the coils. Assume there are two dilute solutions: one is dilute and the other is more concentrated. The concentration of the more concentrated dilute solution can be several times higher than that of the very dilute solution (both solutions are in the dilute solution range). Using these two dilute solutions for self-assembly depositions and keeping all other deposition conditions the same, the number of polyelectrolyte molecules adsorbed by a charged substrate from the more concentrated dilute solution will be several times higher than the number of polyelectrolyte molecules adsorbed from the very dilute solution. After the adsorption process, the adsorbed polyelectrolyte coils will spread because of the repulsion between the same charges on the chains of polyelectrolyte coils and because of the attraction between the opposite charges on the surface of the substrate and on the polyelectrolyte coils. From a thermodynamic point of view, the coils will tend to form a single-chain-layer. If adsorbed coils touch each other before a single chain layer is formed, the spreading of the adsorbed

polyelectrolyte coils will stop to prevent the increase of the energy of the system. Assume the adsorbed polyelectrolytes from the very dilute solution form a single chain layer on the porous substrate; the adsorbed polyelectrolytes from a more concentrated dilute solution will form a layer with a thickness of several chains. By increasing the thickness of each deposited layer, the total number of depositions needed to form a defect-free separating layer can be reduced.

To prove this new concept, two composite membranes were prepared with the two-sided deposition method and the concentration-change deposition technique. One composite membrane was coated with 0.02 monomol/L solutions for the first 2 deposition cycles and then 0.2 monomol/L solutions for the next 4 deposition cycles. This coating process is called (2+4) deposition cycles in this work, which means that dilute solutions were used for the first 2 deposition cycles and more concentrated dilute solutions were used for the additional 4 deposition cycles. The other composite membrane was prepared with (2+8) deposition cycles. The pervaporation performance of these composite membranes is shown in Tables 3-13 and 3-14, respectively.

**Table 3-13. Pervaporation performance of the composite membrane formed with (2+4) deposition cycles [a]**

| Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt%) | Separation factor |
|---|---|---|---|
| 22 | 0.19 | 97.6 | 474 |
| 40 | 0.38 | 98.8 | 960 |
| 50 | 0.50 | 99.6 | 2900 |
| 60 | 0.64 | 100[b] | $\infty$[b] |

[a.] two-sided deposition and water content in feed was 7.9 wt%

[b] the content of IPA was too small to be measured

**Table 3-14. Pervaporation performance of the composite membrane formed with (2+8) deposition cycles [a]**

| Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt%) | Separation factor |
|---|---|---|---|
| 40 | 0.17 | 98.8 | 835 |
| 50 | 0.26 | >99.0 | >1000 |
| 60 | 0.33 | >99.0 | >1000 |

[a.] two-sided deposition and water content in feed was 9.0 wt%.

The composite membrane formed with (2+4) deposition cycles had a total of 24 self-assembled polyelectrolyte layers, while the composite membrane formed with 8 deposition cycles had a total of 32 layers. It can be seen from Tables 3-13 and 3-10 that the composite membrane formed with (2+4) deposition cycles had lower fluxes and higher separation factors than the composite membranes formed with 8 dilute solution deposition cycles though the latter had more layers than the former. This shows that by using the concentration-changing deposition technique, even when the total number of layers in a separating layer had been reduced, the separation performance of the composite membranes obtained still could be improved. Because the concentration of the more concentrated dilute solution used in this work was 10 times larger than the concentration of the dilute solution, the thickness of the single layer formed with the more concentrated dilute solution could be several times larger than that formed with a dilute solution if all other deposition conditions were the same. This explains why the membrane formed with (2+4) deposition cycles had lower fluxes and higher separation factors than the membrane formed with 8 dilute deposition cycles. This shows that it is possible to use the concentration-changing deposition technique to reduce the number of deposition layers required for making a composite membrane.

The data in Tables 3-13 and 3-14 demonstrate that a composite membrane with 10 self-assembled double layers made with the concentration-changing deposition

technique had good separation performance if the two-sided deposition method was used to make the membrane.

To prove that the concentration-changing deposition technique could also be used to reduce the number of layers when the one-sided deposition method was used, two additional composite membranes were made with the one-sided deposition method. One sample was made with dilute solutions with constant concentrations (marked with 10 double layers, which means that all 10 double-layers were made with dilute solutions) and the other one was made with dilute solutions with varying concentrations (marked with 3+7 double layers, which means that the first 3 double-layers were made with dilute solutions, and additional 7 double-layers were made with more concentrated solutions).

In Figure 3-4, the separation performance of the membrane prepared with dilute solutions of same concentrations (□) is compared with that prepared with dilute solutions with varying concentrations (Δ). These two membrane samples were formed using porous PAN substrates that were hydrolyzed at 75$^{O}$C for 30 min and the feed IPA/water mixture used for performance test contained 9.8 wt% of water.

In general, as feed temperature increases, the flux of a pervaporation membrane increases and the separation selectivity of the membrane decreases. Therefore, the feed temperatures in this work were changed from 25$^{O}$C to 70$^{O}$C to study the separation performance of the self-assembled membranes obtained.

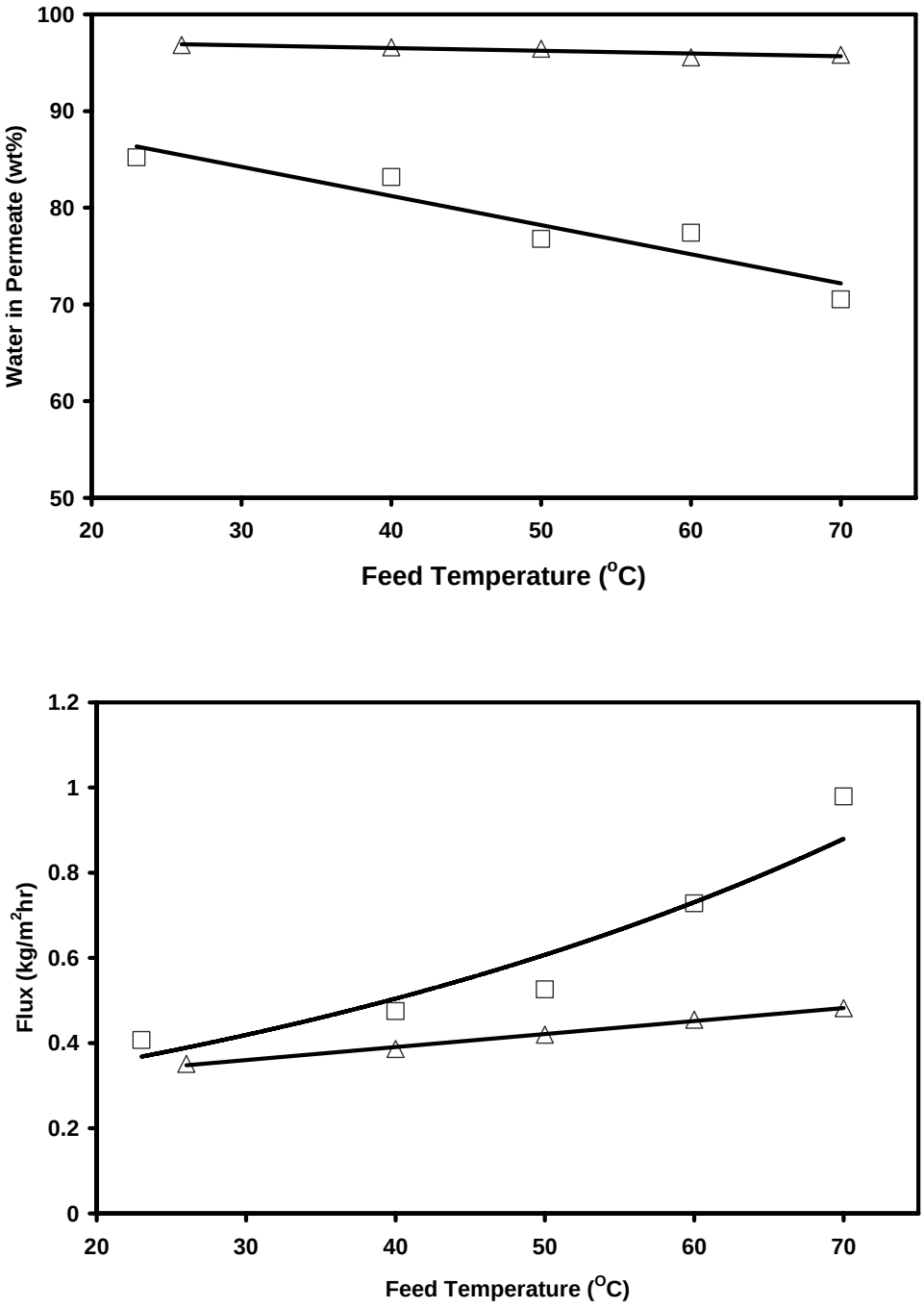



**Figure 3-4. The separation performance of the polyelectrolyte membranes**

□: the membrane made with constant-concentration-depositions (10 double layers)

Δ: the membrane made with concentration-changing depositions (3+7 double layers)

From Figure 3-4, it is clear that with the same number of depositions, the composite membrane made with the concentration-changing deposition technique (3+7 double layers) had higher water concentration in permeate and lower fluxes than the composite membrane made with dilute solutions with constant concentrations under the same experimental conditions. This indicates that the concentration-changing deposition technique could also be used to reduce the number of one-sided depositions needed for making a composite membrane. If the number of depositions was fixed, using the concentration-changing deposition technique would increase the thickness of single deposition layer and the total thickness of the separating layer of a composite membrane. As a result, the flux of this composite membrane so obtained would decrease. Figure 3-4 shows that the idea does work of reducing the total number of depositions by changing the concentrations of deposition solutions when the one-sided deposition method is used for making membranes.

According to the definition of dilute solution, the size of a polyelectrolyte chain in a dilute solution and the size of the same polyelectrolyte chain in a "more concentrated dilute solution" should be the same as long as both solutions are dilute. There is no difference in the conformation of the same polyelectrolyte molecular chain in these two dilute solutions. Yet in the adsorption step of an electrostatic self-assembly process, the conformation of the same polyelectrolyte chain in these two dilute solutions could be different. In a "more concentrated dilute solution," the polyelectrolyte coils that had been adsorbed onto the surface of the substrate previously had more chances to interact with the polyelectrolyte coils in the solution and because of this interaction, the sizes of the polyelectrolyte coils in the solutions could be compressed. A polyelectrolyte molecule that usually could not go into the pore on the porous substrate would go into the pores after the compression. It was favorable to use dilute solutions to cover relatively big pores for the first several depositions on a porous substrate. After several depositions, the pore sizes of the porous substrate had been reduced significantly and "more concentrated dilute solutions" could be applied to make thicker deposition layers. Polyelectrolyte solutions with two different concentrations were selected for depositions in this work. One concentration was 0.020 monomol/L; the other one was 0.20 monomol/L.

Whether a solution is dilute can be determined by evaluating its critical overlapping concentration. The critical overlapping concentration of a polymer solution can be expressed by the following [He et al. 1990]:

$$C^* = \frac{M}{\tilde{N}\rho_2 r^3} \text{ (g/g)} \qquad (3\text{-}9)$$

where M is the molecular weight of a polymer (g/mol), $\tilde{N}$ the Avogadro constant (/mol), $\rho_2$ the solvent density (g/L), and r the radius of gyration of a polymer.

With the estimated $r_o$ calculated using equation (3-8), the unperturbed critical overlapping concentration is estimated to be is 0.11 g/g for poly(acrylic acid) solution if the molecular weight of the poly(acrylic acid) in solution is 250,000.

**Table 3-15. Concentration conversion of poly(acrylic acid) deposition solutions**

| The concentration of poly(acrylic acid) solution (monomol/L) | The concentration of poly( acrylic acid) solution (g/g) |
|---|---|
| 0.010 | 0.0007 |
| 0.020 | 0.0014 |
| 0.20 | 0.014 |

If the concentration of a poly(acrylic acid) (Mw 250,000) solution is 0.020 monomol/L, this poly(acrylic acid) solution is a dilute solution because the concentration of this solution, after conversion, is 0.0014 g/g that is lower than the unperturbed critical overlapping concentration (0.11g/g). If the concentration of a poly(acrylic acid) solution is 0.20 monomol/L and if the molecular weight of the poly(acrylic acid) in the solution is 250,000, this solution is still a dilute solution because the concentration of this solution (0.014 g/g) remains below the unperturbed critical overlapping concentration. We have assumed that the polyelectrolyte in the deposition solution is in an unperturbed condition because we have used the unperturbed radius of gyration to calculate the critical overlapping concentration. However, water is a good solvent for polyelectrolytes and a polyelectrolyte in water is not in an unperturbed condition. The actual size of a

polyelectrolyte coil in water is larger than that in an unperturbed condition, leading to a reduction in the critical overlapping concentration. Nevertheless, 0.020 monomol/L and 0.20 monomol/L poly(acrylic acid) (Mw 250,000) deposition solutions were used in different stages of self-assembly depositions in this work as a dilute solution and a more concentrated dilute solution, respectively.

A higher molecular weight poly(acrylic acid) ($M_w$ =1,000,000) were also used as a polyanion in this work. For the poly(acrylic acid) with a molecular weight of 1,000,000, a 0.20 monomol/L solution would not be a dilute solution because its concentration (0.014 g/g) was equal to the calculated unperturbed critical overlapping concentration (0.014 g/g). A 0.20 monomol/l poly(acrylic acid) solution (Mw 1,000,000) cannot be used for self-assembly depositions because only dilute solutions can be used for self-assembly depositions. When a high molecular weight poly(acrylic acid) was used as a polyelectrolyte to make composite membranes, the concentration of the deposition solution was 0.020 monomol/L.

## 3.3.4 Development of polyelectrolyte self-assembled membranes for pervaporation

### 3.3.4.1 Effect of the pore size of a porous substrate on the number of depositions needed in a composite membrane

To study the effect of the pore size of a porous substrate on the number of depositions needed to make a composite membrane, a porous PAN membrane with nominal MWCO of 30,000 was also hydrolyzed at 75$^{O}$C for 20 min and this hydrolyzed porous PAN membrane was then used as a porous substrate to make a composite membrane with 3+7 deposition cycles. Table 3-16 gives the separation performance of two composite membranes made from two porous substrates having different MWCOs. It was found that when the total number of double layers in the composite membrane was 10, the composite membrane made from a porous substrate with nominal MWCO of

30,000 had a much lower selectivity than the composite membrane made from a porous substrate with a nominal MWCO of 20,000. In order to obtain a similar selectivity, the number of depositions required for a composite membrane using the substrate with MWCO of 30,000 needed to be substantially increased. This demonstrates that the pore size of the porous substrate used significantly affected the number of depositions needed for making an acceptable membrane. This also proves that the pore size of the porous substrate with MWCO of 30,000 was too big if the composite membranes with less than 10 self-assembled double layers needed to be fabricated.

**Table 3-16. Separation performance comparison between two composite membranes made from two porous substrates with different MWCOs (40$^{O}$C)**

| Depositions | MWCO of the substrate | Flux (kg/m$^2$hr) | Water in permeate (wt %) |
|---|---|---|---|
| 3+7 | 20,000 | 0.4 | 96.6 |
| 3+7 | 30,000 | 2.2 | 37.8 |

To understand the effect of the pore size of a selected porous substrate on the number of deposited layers needed for a composite membrane, we need to discuss the penetration of polyelectrolyte molecules in the pores of a porous substrate. When the same polyelectrolyte molecules are used to make self-assembled layers on two porous substrates with different pore sizes, the penetration of polyelectrolyte molecules in the pores of different porous substrates will be different. The smaller the pore size, the more difficult it is for a polyelectrolyte molecule to penetrate into the pores. If the molecular size of the polyelectrolyte is little larger than or similar to the size of the pores on the porous substrate, the polyelectrolyte molecules will be adsorbed onto the inner surface at the entrance of the pores if the polyelectrolyte coils enter the pores. In this case, a few depositions will make the relatively large pores small enough to prevent further penetration of the polyelectrolyte coils, and the porous substrate will become “non-porous”. However, if the pore size is much larger than the size of the polyelectrolyte molecules, the polyelectrolyte molecules will penetrate deep into the pores or even pass

through the pores. In either case, many polyelectrolyte molecules are needed to fill the large pores on the porous substrate to render the substrate "non-porous". In our work, when a hydrolyzed PAN membrane with a MWCO of 20,000 was used as a substrate, few depositions could change the porous substrate into a "non-porous" substrate. However, when a hydrolyzed PAN membrane with a MWCO of 30,000 was used for depositions, many depositions were needed to make the porous substrate "non-porous". The depositions used for filling the pores had little effect on the selectivity of the final membrane. This explains why the separation performance of the composite membrane made from a hydrolyzed porous PAN membrane with a MWCO of 20,000 was much better than that of the membrane made from a hydrolyzed porous PAN membrane with a MWCO of 30,000. In other words, the porous substrate with larger pores needed more filling depositions to become "non-porous", while the number of filling depositions could be remarkably reduced by using a porous substrate with smaller pore sizes.

Based on this, the following self-assembled composite membranes were prepared from the porous PAN membrane with a nominal MWCO of 20,000.

### 3.3.4.2 Effect of drying method on the separation performance of composite membranes

Figure 3-5 shows the effect of the drying method on the separation performance of self-assembled composite membranes at different feed temperatures. After the depositions, the resulting composite membranes contain some water. The membrane samples usually need to be dried before the pervaporation test. This was accomplished in two ways. One way was to dry the membrane sample at room temperature (23-25$^{O}$C), and the evaporation rate of the solvent (water) was relatively low (slow evaporation). The other way was to dry it at an elevated temperature (85$^{O}$C) and the evaporation rate of the solvent was relatively high (fast evaporation). The data in Figure 3-5 show that the membrane dried at room temperature had a higher permeate water concentration and a lower flux than that dried at 85$^{O}$C.

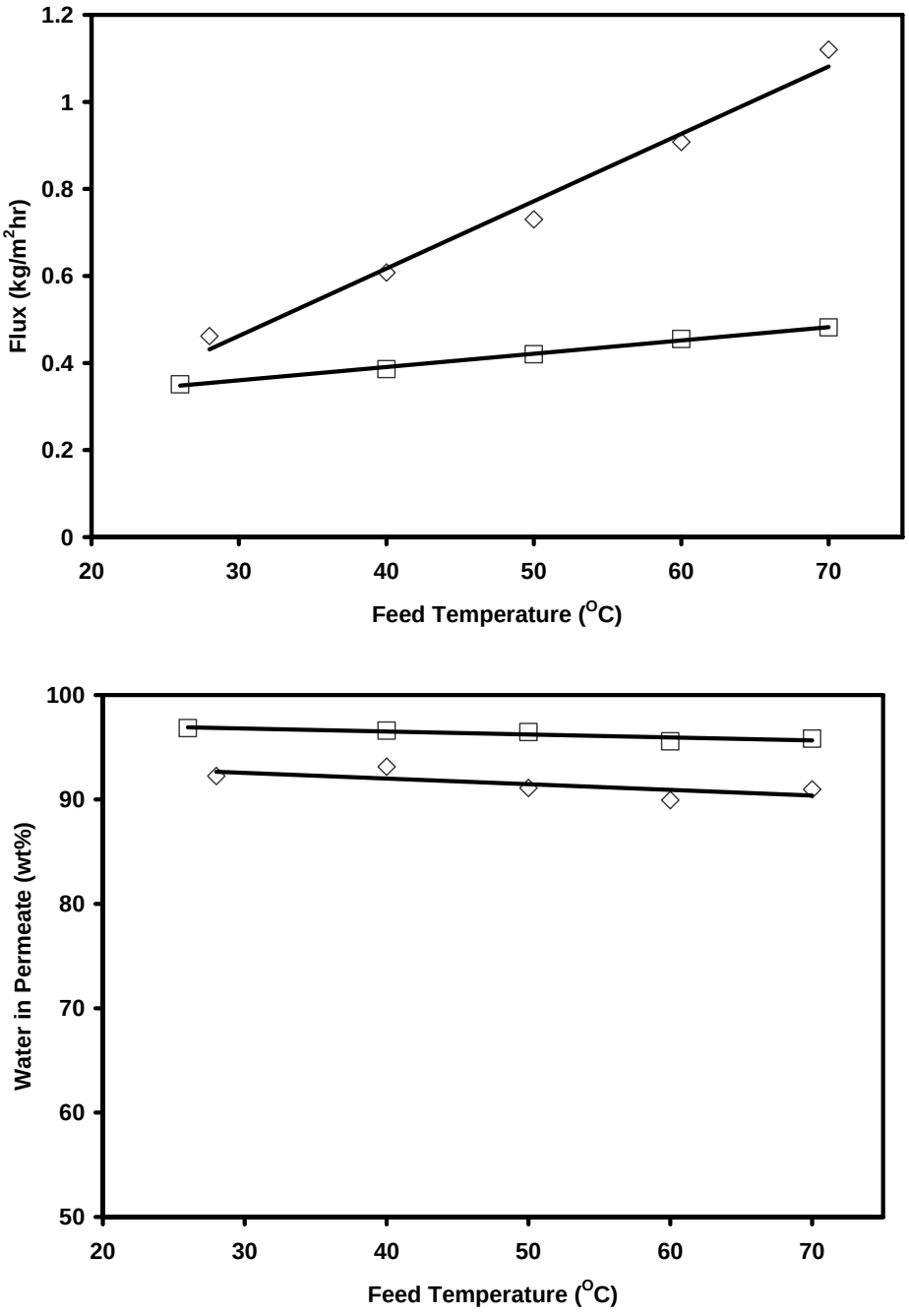



**Figure 3-5. Effect of drying method on the separation performance of the composite membranes (3+7 double-layers) at different feed temperatures**

□: Slow drying (at 25$^{O}$C)  ◊: Fast drying (at 85$^{O}$C)

The separation performance of a composite membrane is determined by its structure and morphology. Different drying conditions will lead to different structures and morphologies in the separating layers. It was noticed that the composite membrane, after being dried at 85$^{O}$C, was not flat anymore but had a certain extent of warpage (the membrane dried at room temperature was still flat). The warpage was an indication of stresses in the membranes. Both a hydrolyzed PAN layer and a polyelectrolyte separating layer were rather brittle in the dry state, and the stresses in the membranes during drying could cause structure defects. When these defects were minor, a composite membrane still had a certain separation function but with a higher flux and a lower selectivity. This trend has been shown in Figure 3-5.

#### 3.3.4.4 Effect of deposition solution pH on the separation performance of composite membranes

It is well known that the pH of a weak polyelectrolyte solution affects the degree of ionization of the polyelectrolyte in the solution. Depending on the pH of the solution, a weak polyelectrolyte can be totally ionized, partially ionized or completely un-ionized, which, in turn, will affect the size of the polyelectrolyte coils in the solution. If a weak polyelectrolyte is fully ionized, the deposition layer has a relatively tight structure with a high degree of physical cross-linking. For partially ionized weak polyelectrolyte, the non-ionized chain segments will be incorporated into the deposited layer structure and the deposited layer will have a low degree of cross-linking. As such, if a given weak polyelectrolyte pair is used for making composite membranes, the composite membranes made from polyelectrolytes with high degree of ionization will have a higher selectivity and a lower flux than the membranes made from polyelectrolytes with low degrees of ionization. Thus, the pH of a deposition solution has a direct effect on the separation performance of the self-assembled membranes obtained.

Krasemann et al. [2001] suggested a formula to calculate the “optimum” pH for self-assembly deposition:

$$pH_{opt} = \frac{pk_a(polyanion) + pk_a(polycation)}{2} \qquad (3\text{-}10)$$

At an optimized pH, both the polycation and polyanion will have relatively high degrees of ionization. At a pH above or below the optimized pH, one polyelectrolyte in the polyelectrolyte complex pair will have a relatively low degree of ionization, and a composite membrane with a low cross-linking density will be formed, leading to poor separation performance.

In this work, poly(acrylic acid) and polyethylenimine were used as a polyelectrolyte pair for the fabrication of composite membranes. The pKa for poly(acrylic acid) is 6.2. The pKa for polyethylenimine cannot be found in the literature. Suh et al. [1994] studied the ionization of polyethylenimine and reported that when the pH was about 5, the degree of ionization of polyethylenimine was about 50%. Based on this, the pH of the polyethylenimine deposition solution used in this work was adjusted to between 5 and 5.5 in order to produce a self-assembled separating layer with high separation performance.

To evaluate the effect of the pHs of deposition solutions on the separation performance of the composite membrane obtained, three different pH conditions were tried: (1) adjust both poly(acrylic acid) and polyethylenimine solutions to pH 3.0; (2) adjust both solutions to pH 5.5; (3) without any pH adjustment (the pH of the poly(acrylic acid) solution is about 6.2 and the pH of the polyethylenimine solution is about 11). Figure 3-6 shows a comparison of the separation performance of self-assembled composite membranes made under these different pH conditions.

When the pHs of deposition solutions were 5.5, the obtained membrane had a lower flux and a higher selectivity than the other two membranes formed with the deposition solutions either without pH adjustment or with pHs adjusted to 3.0. From the degree of ionization of a weak polyelectrolyte at different pH values, the results shown in Figure 3-6 can be elucidated. When the pHs of deposition solutions were 5.5, both polycation and polyanion had relatively high degrees of ionization. There were more electrostatic interactions between oppositely charged polyelectrolytes at pH of 5.5 than at

the other two pH conditions. Hence, the composite membrane formed at pH 5.5 had a smaller molecular weight between cross-link points and a higher degree of cross-linking. Therefore, the "mesh size" of polyelectrolyte network in the composite membrane would be smaller and the separation performance of the membrane would be better. Thus, the membrane obtained had a higher selectivity and a lower flux. When the pHs were adjusted to 3.0, the degree of ionization of poly(acrylic acid) was quite low; when there was no pH adjustment, the degree of ionization of polyethylenimine was quite low. In either case, the separating layer formed would have a low degree of cross-linking and the selectivity of the membrane fabricated in this way would be low. Hence, the pHs of poly(acrylic acid) and polyethylenimine deposition solutions in this research were adjusted to about 5.5 to improve the separation performance of final membranes.

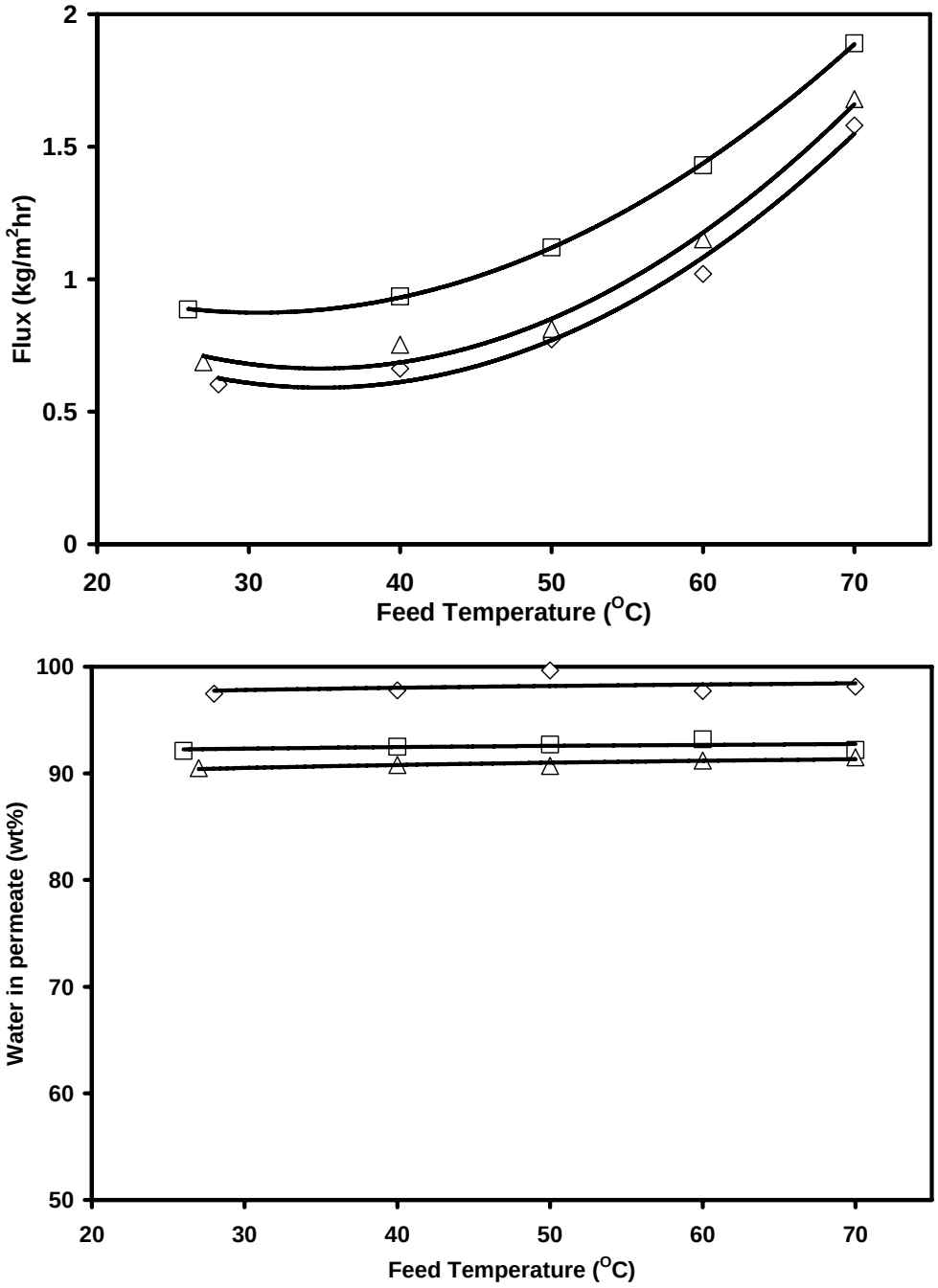



**Figure 3-6. The separation performance of the composite membranes made from polyelectrolyte deposition solutions at different pHs**

◊: pH 5.5 □: No pH adjustment Δ: pH 3.0 (3+7)depositions

### 3.3.4.5 Fabrication of self-assembled membranes

As shown previously, the number of double layers needed for making a composite membrane could be reduced to 10 with one-sided depositions at room temperature using concentration changing technique. However, the fabrication of such a composite membrane was still time-consuming. To further reduce the number of depositions, a high molecular weight poly(acrylic acid) ($M_W$ =1,000,000) was used and some membrane preparation conditions were further fine-tuned. The one-sided deposition method that had been used before was to deposit polyelectrolytes onto a substrate at room temperature with a bottle deposition technique, and this one-sided deposition method was termed a simple one-sided deposition method. In contrast to this, a new one-sided deposition method was proposed. In the new one-sided deposition method, a deposition would be carried out at $50^{O}$C with a bottle deposition technique. This new one-sided deposition method was obtained by modifying the deposition temperature used in a simple one-sided deposition method and therefore was termed as modified one-sided deposition method. All the composite membranes would be made with the modified one-sided deposition method unless specified differently.

In order to get self-assembled membranes with good separation performance, some other membrane preparation conditions have also been changed. For example, the pH of polyethylenimine solution would be adjusted to about 5 and there was no pH adjustment with poly(acrylic acid) solution, and membrane post-treatment would be conducted at $50^{O}$C. Table 3-17 lists all the pre-selected membrane preparation conditions that would be used to fabricate self-assembled membranes hereafter.

All these preparation conditions were chosen based on the parameters reported in the literature and preliminary work carried out in our laboratory.

**Table 3-17. Pre-selected preparation conditions for making composite polyelectrolyte pervaporation membranes**

| | | |
|---|---|---|
| Hydrolysis of PAN (MWCO 20,000) | | $75^{O}$C, 20 min |
| Polyelectrolyte | Polycation | Polyethylenimine Mw 750,000 |
| | Polyanion | Poly(acrylic acid) Mw 1,000,000 |
| Deposition conditions | Temperature | $50^{O}$C |
| | Time | 30 min |
| Post-treatment conditions | Temperature | $50^{O}$C |
| | Time | 12 hr |
| Deposition solution (0.02monomol/L) | | Fresh |
| Deposition method | | Static |

Using the modified preparation conditions, a composite membrane with 7-double-layers was successfully fabricated. Figure 3-7 shows the separation performance of this composite membrane. At $25^{O}$C, a permeate water concentration of more than 90.0 wt% was achieved. When the pervaporation temperature was $70^{O}$C, the water content in permeate was over 98.0%. However, the composite membrane with 7-double-layers still did not have a high flux as compared with commercial PVA membranes.

As pointed out before, when a high molecular weight poly(acrylic acid) (Mw 1,000,000) was used for depositions, a 0.20 monomol/L poly(acrylic acid) solution could not be used for self-assembly because it was not a dilute solution anymore. It was found from Figure 3-7 that when a high molecular weight poly(acrylic acid) was used, there was no need to use the concentration-changing deposition technique to reduce the number

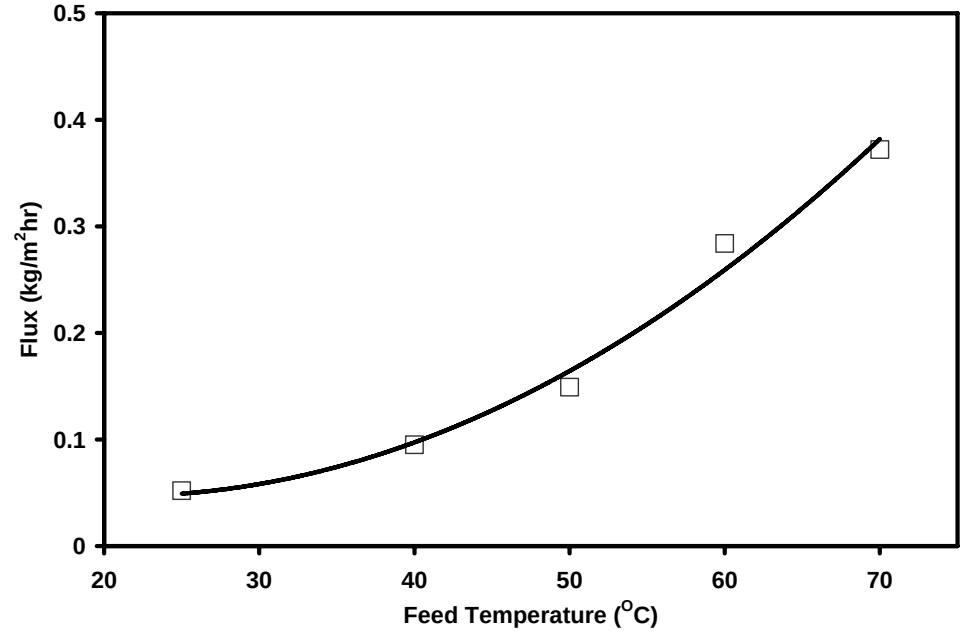
of deposition layers in a composite membrane because 7 self-assembly deposition cycles with dilute deposition solutions (0.02 monomol/L) could give a composite membrane acceptable separation performance.

Self-assembled composite membranes with different numbers of double layers have been fabricated using the fabrication conditions listed in Table 3-17. Figure 3-8 shows the effect of the number of deposition cycles at different feed temperatures on the separation performance of the composite membranes. The number of deposition cycles required for self-assembled composite membranes are further reduced in Figure 3-8. Figure 3-8 shows that if a suitable porous substrate and suitable polyelectrolytes were used for the fabrication of composite membranes, the number of deposition cycles required for self-assembled composite membranes could be as low as 2 and the obtained composite membrane still had good separation performance.

If the thickness of each individual polyelectrolyte layer is the same, as the number of double layer increases, the flux of the composite membrane will decrease. Applying the resistance-in-series model to the separating layer in a composite membrane, we have

$$R_P = \Sigma R_i \quad (i=1,\ldots n) \qquad (3\text{-}11)$$

where $R_i$ is the mass transport resistance of the i-th polyelectrolyte double layer and n is the number of double layers in a polyelectrolyte separating layer, i.e. half of the total number of depositions needed for making a separating layer. Reducing the number of deposition layers will reduce the total mass transport resistance and thereby increase the flux of the composite membrane obtained. As to the selectivity, the selectivity of the composite membrane will increase as the number of layers increases. It is interesting to notice that all the composite membranes with different numbers of layers had high selectivities after the pervaporation test had been run for several hours. When feed temperature was $70^{O}$C, all permeate samples contained more than 98.0 wt% of water. There were some membranes that, at the beginning of the pervaporation test, did not give



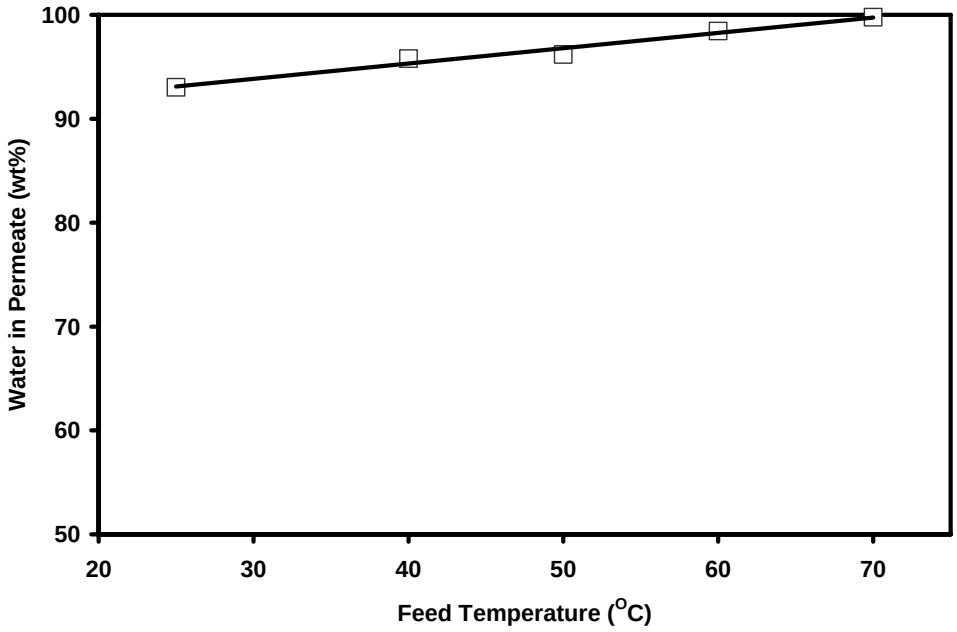




**Figure 3-7. The separation performance of the composite polyelectrolyte pervaporation membranes with 7 double-layers**

high water concentrations in permeates. This might be attributed to some minor defects in the separating layers of these composite membranes. As the pervaporation process proceeded, the polyelectrolyte molecules in the separating layers changed their conformations and the minor defects could be self-cured. As a result, the water content in permeate would increase as pervaporation continued. When a composite membrane with 2 double layers was used for the dehydration of IPA/water (91.0/9.0 in wt) mixture at $70^{O}C$, the flux was above 1.5 $kg/m^2hr$ and the water concentration in permeate was over 98.0 wt%.

These results demonstrate that it was possible to make self-assembled composite membranes with reduced number of self-assembled double layers for the dehydration of IPA/water mixtures.

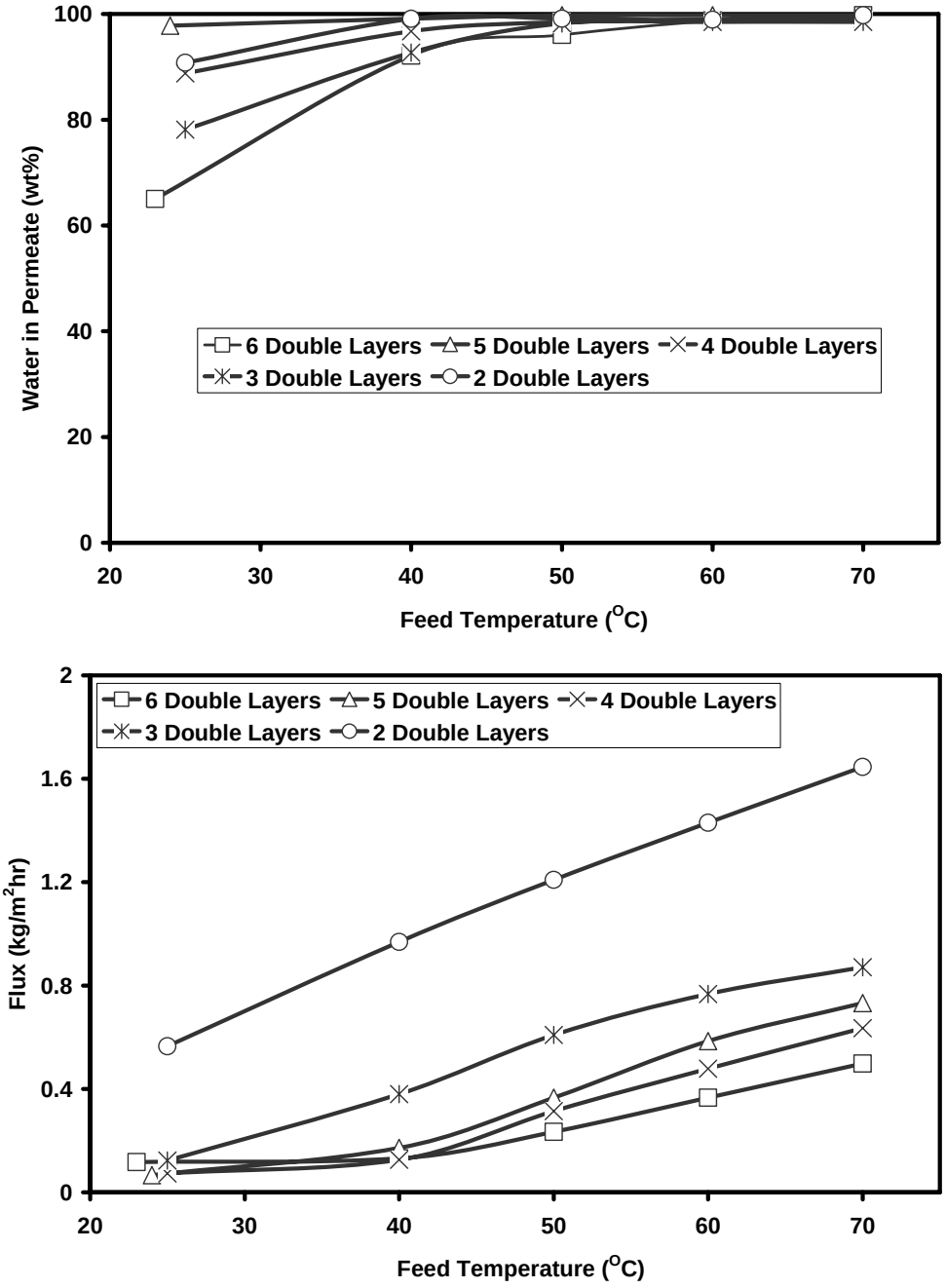



**Figure 3-8. Effect of the number of depositions at different feed temperatures on the separation performance of the composite membranes**

## 3.4 Qualitative considerations concerning the formation of a multilayer on a porous substrate

Tsukruk et al. [1997] studied the formation of a polyionic monolayer built by an electrostatic self-assembly deposition on a charged non-porous surface. By observing the monolayer at different stages in the deposition process, they found that the monolayer made by a self-assembly deposition was not homogeneous at an early stage. At the beginning, the electrostatic adsorption of polyelectrolytes was predominant and the chains of polyelectrolyte molecules were tethered to the charged surface by a few segments and thus to preserve their coiled conformations at this stage. As deposition continued, the polyelectrolyte molecular chains that had been adsorbed previously by the substrate changed their conformations from a three dimensioned coil to a two dimensioned layer. When the deposition time was long enough (usually > 10 min), the structure of adsorbed polyelectrolytes tended to reach equilibrium and a homogeneous polyelectrolyte layer composed of highly flattened polyelectrolyte chains was formed. Based on these observations, they suggested that the deposition of a polyionic monolayer on a charged non-porous surface was a two-step process. The polyelectrolyte chains were first adsorbed by the surface with opposite charges, and then the absorbed polyelectrolyte chains spread over the charged surface. This two-step mechanism has been supported with the results from Mcaloney & Goh [1999]. Two-step process is the mechanism of the formation of a polyionic monolayer on a non-porous substrate.

Recently, Nguyen et al. [2004] investigated the mechanism of the immobilization of bio-macromolecules onto membranes via an adsorbed nanolayer. They used a porous material with fine pores (pore size ranging from 1.9 - 4.1 nm in wet form) to make a self-assembled polyelectrolyte nanolayer to immobilize bio-macromolecules. Their interest was in the mechanism of the deposition of bio-macromolecules onto the charged self-assembled nanolayer that was basically non-porous, and their work was related to the

self-assembly deposition on a non-porous nanolayer (although they did use a porous substrate at the beginning of their research).

Tieke's group has done extensive work utilizing self-assembly techniques to make polyelectrolyte composite membranes for pervaporation [Klitzing and Tieke, 2004]. They used a plasma-treated porous PAN membrane as a substrate for the fabrication of a composite membrane, and Figure 2-4 has been used to schematically explain the deposition of a polyelectrolyte chain on a porous substrate via electrostatic self-assembly. Strictly speaking, the mechanism illustrated in Figure 2-4 is for the self-assembly on a non-porous substrate because the sizes of the polyelectrolytes considered are much larger than the pore size on the porous substrate. As a result, the porous substrate actually behaves like a non-porous substrate from a polyelectrolyte deposition point of view.

Although the formation of self-assembled deposition on a non-porous substrate has been studied in a few publications, there is no information in literature about the formation of a self-assembled multilayer on a porous substrate.

A more accurate picture about the formation of a self-assembled multilayer on a porous substrate will be qualitatively considered in this section.

### 3.4.1 The penetration of polyelectrolytes in a porous substrate

Depending on the molecular sizes and the pore size of a porous substrate, polyelectrolytes can penetrate the porous substrate to different degrees in a deposition process. The study of the penetration of polyelectrolyte molecules in a porous substrate has been totally neglected in the literature despite that many results show the existence of the penetration. When a polyelectrolyte deposits on a non-porous substrate, the polyelectrolyte chain has nowhere to go but deposits on the surface of the substrate. However, when a porous substrate is used for deposition, polyelectrolyte chains can enter the pores of the substrate or pass through the pores. This is the reason why Tieke's membranes needed 60 double layers while Meier-Haack's membranes needed only

several depositions to achieve a reasonable selectivity. It was reported that the amount of polyelectrolytes adsorbed per deposition cycle on a porous support was considerably larger than that on a pore-free substrate [Tieke et al., 2001]. A porous substrate cannot adsorb more polyelectrolytes than a non-porous substrate because the latter has more area for adsorption on the surface of the substrate than the former under the same conditions. Only when the inner surfaces of the pores on a porous substrate also adsorb polyelectrolytes or when the polyelectrolytes pass through the pores on a porous substrate, can a porous substrate "adsorb" more polyelectrolytes than a non-porous substrate.

It has been noticed that, during the experiments of this work, a composite membrane with a porous substrate having a MWCO of 30,000 needed more depositions to achieve the same selectivity as a composite membrane with a porous substrate having a MWCO of 20,000. It is well known that the composition and the quantity of the permeate passing through the first double layer of a self-assembled separating layer is exactly the same as that passing through the last double layer in a continuous and steady process. That a certain number of double layers is needed to make a membrane with given separation performance means that a certain number of double layers is needed to make a "perfect" double layer with given separation performance. In other words, there is only one "perfect" double layer in "a certain number of double layers" and the other double layers are ineffective ones. Thus, the fact that more double layers were needed to obtain a "perfect" double layer when the MWCO of the substrate changed from 20,000 to 30,000 indicates that more depositions were needed to "plug" all the pores to obtain the same selectivity if the pore size of a porous substrate increased.

The penetration of polyelectrolyte molecules in a porous substrate is important because it directly affects the formation of a self-assembled polyelectrolyte multilayer on a porous substrate and the number of double layers required in a self-assembled composite membrane. Before the formation of a self-assembled multilayer on a porous substrate is discussed, the penetration of polyelectrolyte molecules in a porous substrate needs to be discussed first.

Based on the relative size of polyelectrolyte to the pore on a porous substrate, the following different cases can be considered.

Case 1: When the molecular size of a polyelectrolyte in a deposition solution is much larger than the size of the pores on a porous substrate, the polyelectrolyte coil in the deposition solution will not enter the pores. Even if a small portion of a polyelectrolyte coil can still enter the pores of a porous substrate, the penetration of the polyelectrolyte molecules in the porous substrate is insignificant and negligible.

Case 2: When the molecular size of a polyelectrolyte in the deposition solution is little larger than or similar to the size of the pores on the porous substrate, the polyelectrolyte molecules can either cover the pores or go into the pores. If a polyelectrolyte molecule does go into a pore, it will not penetrate deep into the pore because it will be adsorbed onto the inner surface at a place near the entrance of the pore. Because of the adsorption inside the pores, the effective pore size will be decreased. After subsequent depositions of polyelectrolytes, the pores on the porous substrate will become so small that polyelectrolyte coils can no longer enter them. The initial porous substrate has now become "non-porous". In this case, the penetration of polyelectrolyte molecules in the porous substrate is limited and a few self-assembly depositions will prevent this penetration.

Case 3: When the molecular size of a polyelectrolyte in the deposition solution is smaller than the pore size, the polyelectrolyte molecule will go into the pore easily. The polyelectrolyte molecule can be adsorbed onto the inner surface of the pores at any place between the entrance and the exit of the pores. The smaller the molecular size of the polyelectrolyte, the deeper it will penetrate. If the molecular size of the polyelectrolyte is small enough, the polyelectrolyte can "leak" through the pore. In this case, the penetration of polyelectrolyte molecule in the pores is significant and many polyelectrolyte depositions will be needed to make the substrate non-porous.

Although small size polyelectrolyte molecules can easily enter the pores of a porous substrate, it is difficult for them to pass through the pores of a charged porous

substrate because of the electrostatic interactions. The electrostatic interaction distance needs to be taken into consideration when a polyelectrolyte coil goes into the pores of a porous substrate with opposite charges. If the distance between the opposite charges is short enough, the polyelectrolyte coil will be adsorbed onto the inner surface of the porous substrate. Otherwise, the polyelectrolyte coil will pass through the pore of the porous substrate. The effective coil size of the polyelectrolyte molecule in the deposition on a porous substrate with opposite charge consists of an expanded coil size (because of the repulsion between the same charges) plus the electrostatic interaction distance (Figure 3-9). The effective coil size of a polyelectrolyte molecule is definitely larger than that of a non-polyelectrolyte with similar molecular weight, and it is therefore relatively difficult for a polyelectrolyte coil to pass through an oppositely charged pore on a porous substrate.

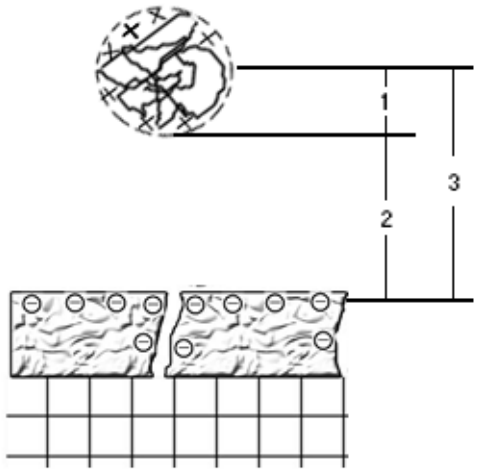



**Figure 3-9. Effective coil size of a polyelectrolyte molecule**

1. Coil size. 2. Electrostatic interaction distance. 3. Effective coil size

Most of the polyelectrolyte molecules, after going into the pores on a porous substrate, will be adsorbed by the inner surface of the pores if the pore size is not too large. Because of the adsorption on the inner surface of the pore, polyelectrolyte molecules can fill the pores. By repeated filling depositions of polycation and polyanion

molecules alternatively, the pore size of a porous substrate will be decreased and the penetration of polyelectrolyte molecules in a porous substrate will be eventually stopped.

### 3.4.2 The formation of a self-Assembled multilayer on a porous substrate

Considering the penetration of polyelectrolyte molecules in a porous substrate, the formation of a self-assembled multilayer on a porous substrate also can be divided into three cases.

Case 1: The penetration of polyelectrolyte molecules in the porous substrate is negligible. Because the sizes of polyelectrolytes are much larger than pore size on the porous substrate, most polyelectrolyte coils will form layers in deposition processes to cover the surface of the porous substrate. The self-assembly depositions on such a porous substrate are essentially the same as the self-assembly depositions on a non-porous substrate. This is an ideal case of a self-assembly on a porous substrate. This is the case depicted in Figure 2-4.

Case 2: The penetration of polyelectrolyte molecules in the porous substrate is limited. The sizes of polyelectrolyte molecules are few times larger than the pore size on the porous substrate. Polyelectrolyte molecules have relatively small chances to go into the pores. Even if some polyelectrolyte molecules do go into the pores, they will be adsorbed by the inner surface of the pores. Some small pores can thus be covered by a single deposition, and other pores may be covered by a few additional depositions. After a few depositions, all the pores will become so small that polyelectrolyte molecules cannot enter them anymore. Subsequent depositions are essentially depositions on a psudeo-non-porous substrate. In this case, a few depositions are needed first to make the substrate “non-porous”, and then a self-assembled multilayer can be built on this “non-porous substrate”. The present work belongs to case 2. The formation of a self-assembled multilayer for this case is shown schematically in Figure 3-10.

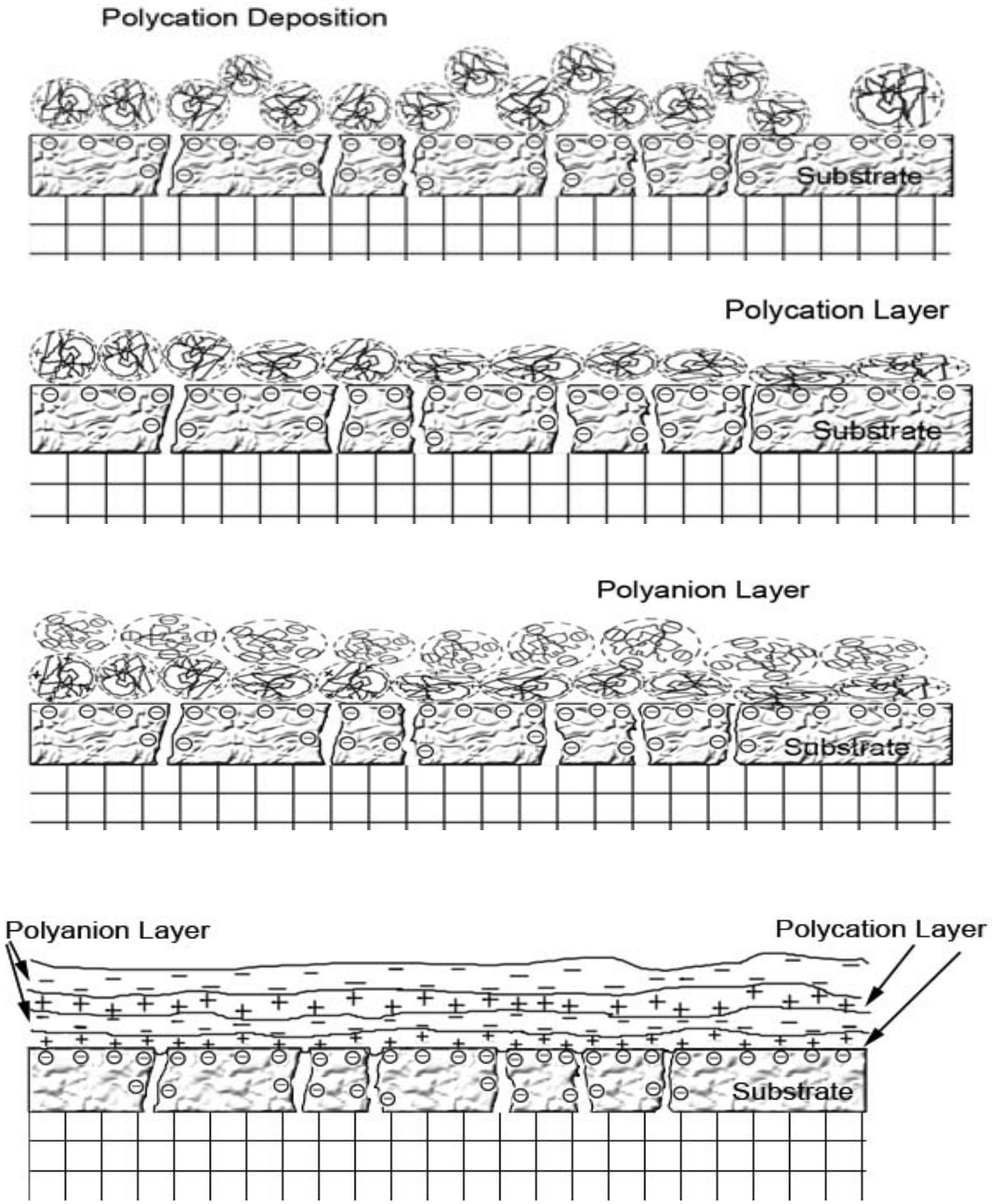



**Figure 3-10. The formation of a self-assembled separating layer in this work**

Case 3: The penetration of polyelectrolyte molecules in the porous substrate is significant. If the molecular sizes of the polyelectrolytes are relatively small and the pore size of the porous substrate is relatively large, polyelectrolyte molecules can easily go deep into the pores and even pass through the pores. It will take many depositions to fill the large pores on the porous substrate to make a non-porous substrate. Self-assembled depositions over the pores will not happen until the pore size becomes smaller than the molecular sizes of polyelectrolytes used. It is clear that without the filling depositions of polyelectrolyte molecules in the pores, it would be impossible to make a self-assembled multilayer on a porous substrate. The fabrication of Tieke's composite membrane is believed to be this case where the membrane was formed using relatively low molecular weight polyelectrolytes and with a porous substrate having large pores. The structure of the multilayer formed in this case is shown in Figure 3-11.

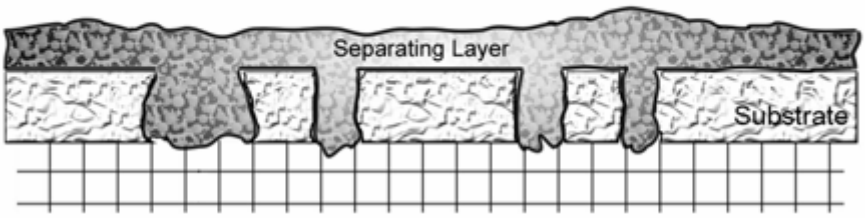



**Figure 3-11. Schematic of structure of a self-assembled multilayer formed with small molecular weight polyelectrolytes and a porous substrate with large pore size**

Because different numbers of filling depositions are needed in different cases to make the porous substrate "non-porous", the numbers of double layers needed in different cases for the membranes with similar selectivities will be quite different. For example, 10 double layers may result in a very high selectivity in case 1, while in case 3, the substrate may still be porous after 10-double-layer-depositions and the selectivity of the membrane obtained is still very poor. This explains why the composite membranes

developed in this work only needed less than 10 self-assembled double layers to get good separation performance while Tieke's membranes needed over 60 double layers.

It is possible to build a single self-assembled polyelectrolyte layer on a porous substrate in case 1, but it is difficult to build a single self-assembled polyelectrolyte layer on the porous substrate in cases 2 or 3 because polyelectrolyte molecules can go into the pores on the porous substrate and the single layer obtained will be porous. In cases 2 or 3, a self-assembled polyelectrolyte multilayer only can be built by initial filling depositions that make the substrate "non-porous" and by followed depositions on this "non-porous substrate". Thus, the formation of a self-assembled multilayer on a porous substrate can be considered to be a two-stage process.

In the first stage, some polyelectrolyte molecules deposit on the "non-porous" portion of a porous substrate, and some polyelectrolyte molecules go into the pores and fill the pores if the pore sizes are larger than the sizes of the polyelectrolyte molecules. There is no integral deposition layer over the surface of the porous substrate until all the pores on the porous substrate become sufficiently small that the polyelectrolyte molecules can no longer go into them. The number of filling depositions needed to make the porous substrate "non-porous" depends on the pore sizes of the porous substrate and the molecular sizes of polyelectrolytes.

In the second stage, the polyelectrolyte molecules cannot enter the pores anymore and the depositions on the porous substrate are similar to the depositions on a non-porous substrate. In this way, a self-assembled multilayer can be built on a porous substrate.

A non-porous substrate can be considered to be a special case of a porous substrate. Therefore, the two-stage process of the formation of a self-assembled multilayer on a porous substrate proposed here can be considered as a general case for the formation of a self-assembled multilayer on either a porous or a non-porous substrate.

## 3.5 Summary

1. A hydrolyzed porous PAN membrane could be used as a porous substrate to make composite polyelectrolyte membranes using the electrostatic self-assembly technique.
2. The concentration-changing deposition technique was shown to be a useful technique to reduce the number of depositions needed for making self-assembled composite membranes.
3. By using a porous substrate with a relatively small pore size and polyelectrolytes with high molecular weights, it was possible to make composite membranes with less than 10 self-assembled double layers.
4. With suitably selected materials and fabrication conditions, self-assembled polyelectrolyte membranes with the number of double layers ranging from 2 to 7 have been fabricated.
5. A two-stage process was suggested to describe the formation of a self-assembled multilayer on a porous substrate.

# CHAPTER 4

# REPRODUCIBILITY STUDIES OF THE COMPOSITE MEMBRANES

## 4.1 Objectives

Composite polyelectrolyte membranes with 60 self-assembled double-layers have been reported by Krasemann et al. [2001]. Because the fabrication of these reported composite polyelectrolyte membranes is time-consuming from an industrial manufacturing point of view, it is necessary to develop a simplified fabrication process to make these composite membranes. Composite membranes with less than 10 self-assembled double layers have been successfully developed in the previous chapter with pre-selected fabrication conditions. The lowest number of the self-assembled double layers in the separating layer of a polyelectrolyte composite membrane is as low as 2, and the process of fabricating composite membranes has been remarkably simplified because of the reduced number of self-assembled double layers. Preliminary experimental results showed that all these composite membranes had fairly good dehydration performance for IPA / water mixtures. The reproducibility of these membranes and the stability of these membranes have not been studied systematically. In this chapter, the dehydration performance of different composite membranes that were made under the same conditions will be determined and compared to study the reproducibility of the composite

membranes with less than 10 self-assembled double layers. In addition, the dehydration performance of a selected composite membrane will also be determined repeatedly to examine the stability of the composite membrane.

# 4.2 Results and Discussion

## 4.2.1 Separation performance of composite membranes made with the same batch of hydrolyzed porous PAN membrane

Figure 4-1 shows the dehydration performance of three composite membranes that have 7 self-assembled double layers. All three composite membranes were made with the same batch of hydrolyzed porous PAN membrane. From Figure 4-1, it is clear that the fluxes of different composite membranes that had 7 self-assembled double layers had relatively large deviations from each other and the water concentrations in permeates also had relatively large deviations. For example, the highest flux among these three membranes, for a given feed temperature ($70^{O}C$), was about 0.75 $kg/m^2hr$ while the lowest was about 0.45 $kg/m^2hr$. At $25^{O}C$, the water concentrations in permeates could change from about 86% to over 98%. The reproducibility of the separation performance of the composite membranes for IPA dehydration is shown in Figure 4-2, where the reproducibility of the separation performance is expressed with averages and data ranges. The size of a data range sometimes cannot express how large the deviation actually is because the data range only tells us how far an individual datum is from an average. For example, for the three composite membranes mentioned above at temperature of $70^{O}C$, the size of the flux data range was only 0.3 $kg/m^2hr$. But when the average flux (0.6 $kg/m^2hr$) was taken into consideration, 0.3 $kg/m^2hr$ stood for a 50 % deviation or a maximum relative error of over 25%. It is obvious that the flux reproducibility of a single composite polyelectrolyte pervaporation membrane with 7 double layers was not good but it was still acceptable from an industrial point of view.

The reproducibility of the dehydration performance of the composite membranes with 2 self-assembled double layers is similar to that of the composite membranes with 7 double layers. Figure 4-3 is the separation performance of three composite membrane samples with 2 double layers. The maximum relative error of the flux of the composite membranes with 2 self-assembled double layers was also about 25% and the reproducibility of the composite membranes with 2 double layers was also barely acceptable.

It is well known that the amount of materials that pass through a transport media depends on the thickness of the media. To explain the relatively low flux reproducibility of the composite membranes with less than 10 self-assembled double layers, it is necessary to discuss the reproducibility of the thickness of a self-assembled double layer.

When a non-porous substrate is used for the deposition of polyelectrolytes using the electrostatic self-assembly technique, the thickness of each polyelectrolyte double layer can be well controlled, and this has been demonstrated by many publications. Even so, the thickness of a self-assembled multilayer deposited on a smooth and non-porous substrate is still different from point to point. A recent publication by Jiang et al. [2004] showed that when 7 self-assembled double layers were deposited on a non-porous substrate to form a multilayer structure, the relative error in the thickness of the multilayer structure was roughly 25%. When a porous substrate is used for the construction of a polyelectrolyte separating layer for a composite membrane, the precise control of the thickness of a multilayer having less than 10 self-assembled double layers is very difficult, if not impossible, because the polyelectrolyte molecules can enter the pores on the substrate. Although a porous substrate with a relatively small pore size and polyelectrolytes with relatively large molecular sizes were intentionally used in this work to prevent the polyelectrolyte molecules from penetrating the pores on the porous substrate, certain polyelectrolytes with relatively small molecular sizes still could enter the pores because the polyelectrolyte molecules used always have a molecular weight

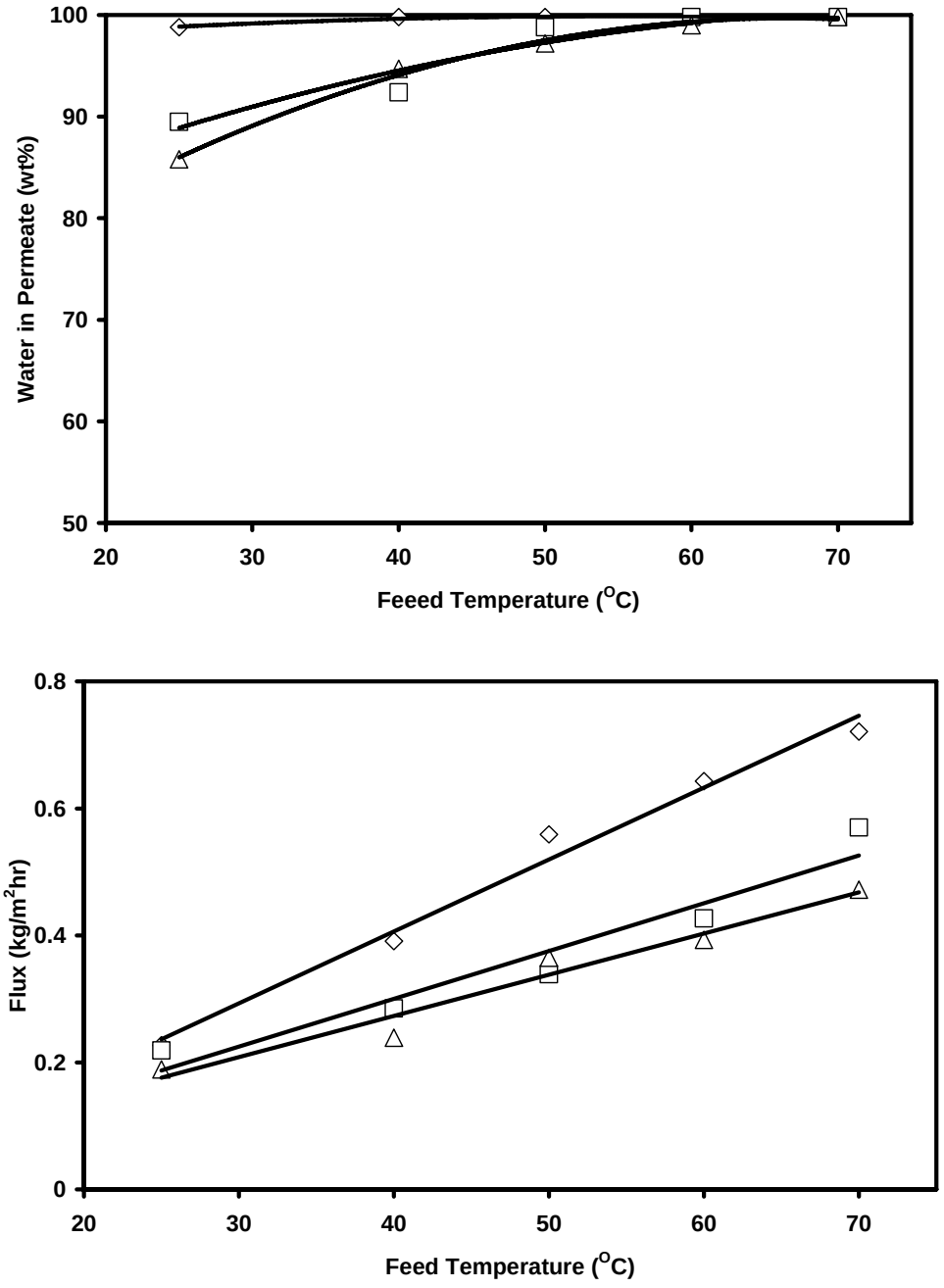



**Figure 4-1. The separation performance of the composite membranes with 7 double layers (group 1)**

◊: Sample 1 □: Sample 2 Δ: Sample 3

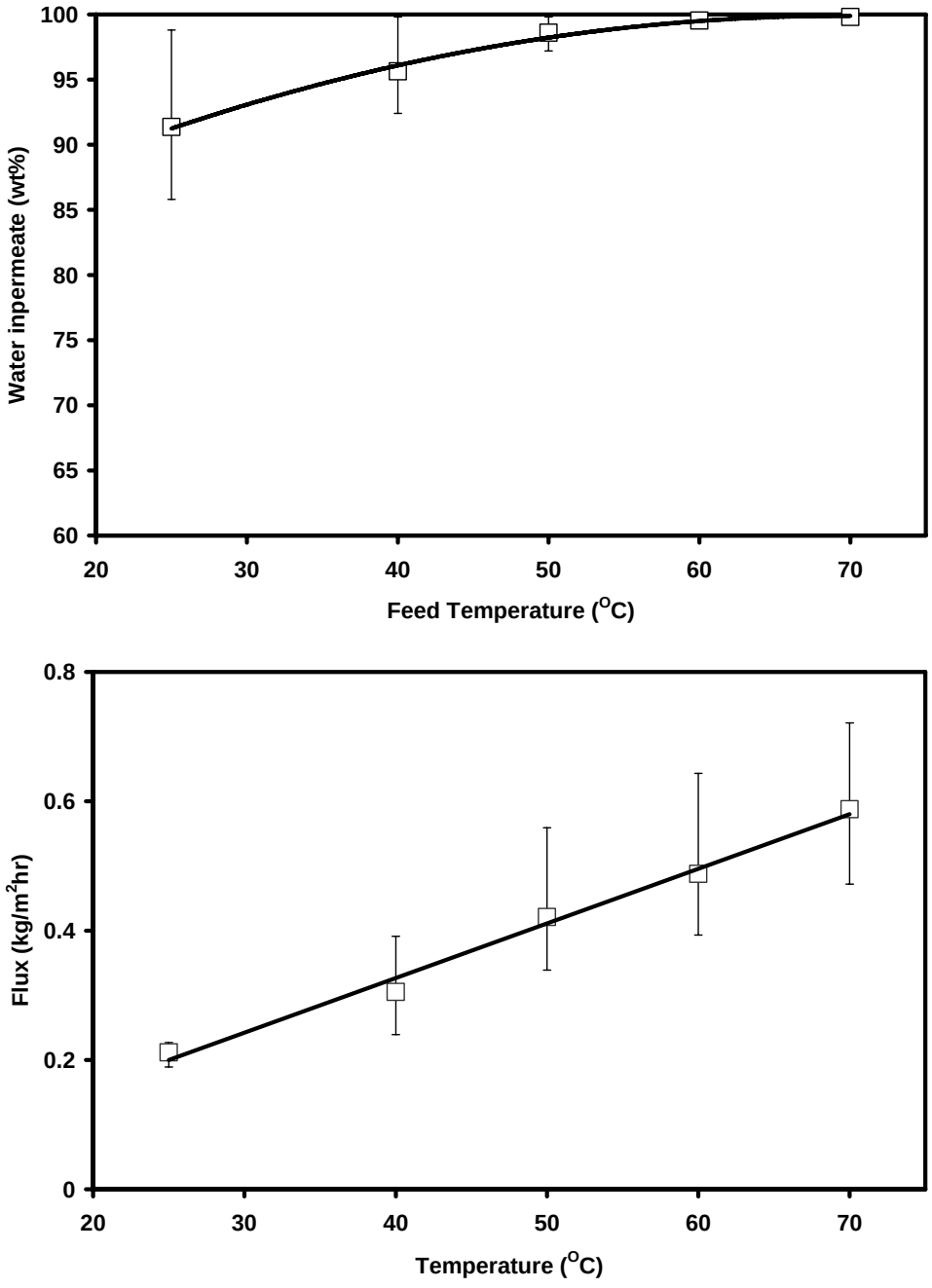



**Figure 4-2. Reproducibility of the separation performance of the composite membranes with 7 double-layers (group 1)**

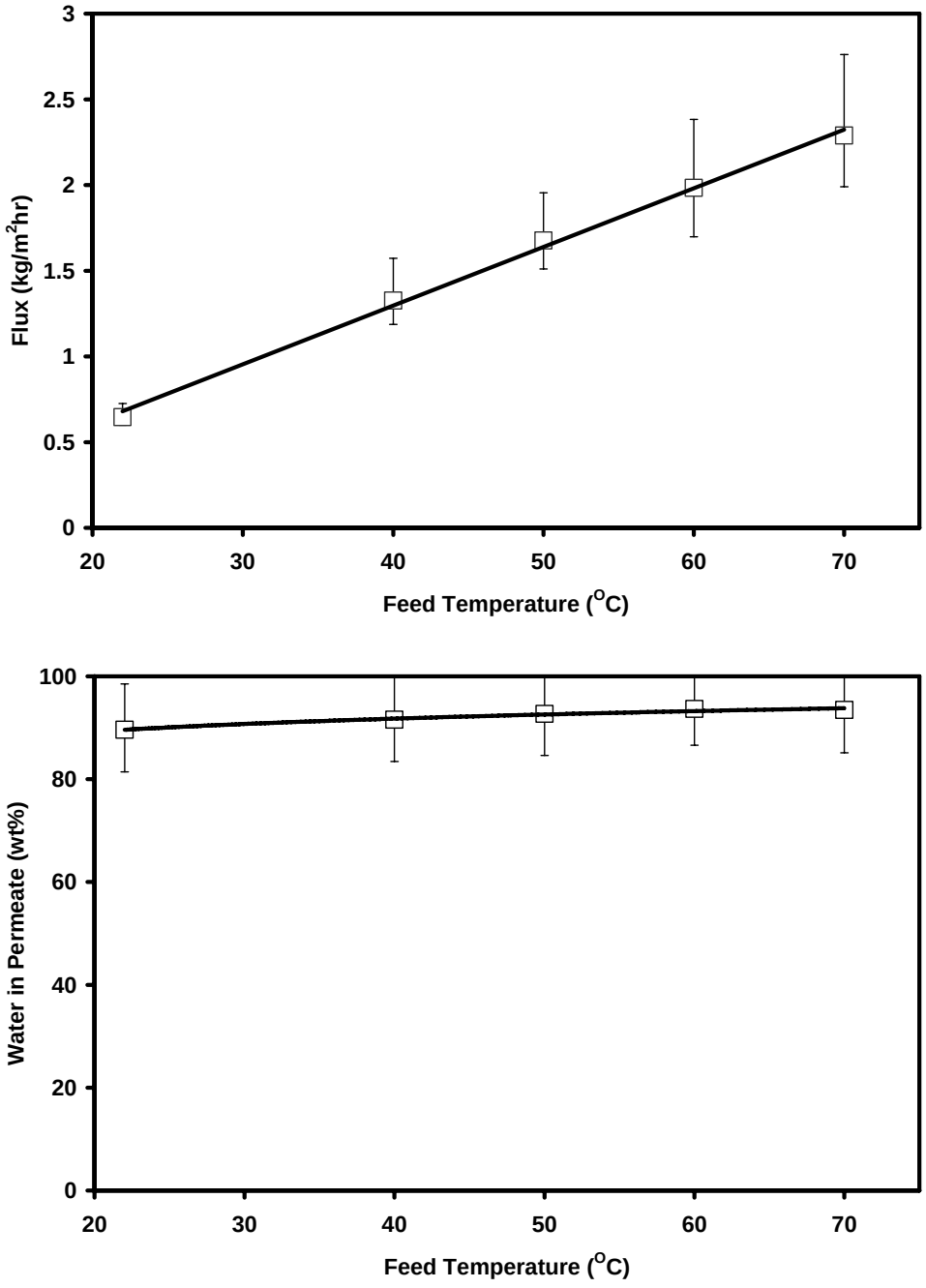



**Figure 4-3. Reproducibility of the separation performance of the composite membranes with 2 self-assembled double layers**

distribution or a molecular size distribution. Assuming all the polyelectrolyte molecules have the same size and the molecular size is several times larger than the pore size on a porous substrate, one polyelectrolyte molecule then can cover more than one pore on the substrate. Even so, the edge of this large polyelectrolyte coil still can go into a pore that is much smaller in size than the polyelectrolyte molecule. From this perspective, the complete prevention of penetration of polyelectrolyte molecules in the pores of the porous substrate is impossible. As the pore size increases, the possibility for a polyelectrolyte coil to enter the pore will increase. When the polyelectrolyte molecules do go into the pores, the thickness of the self-assembled multilayer over the pores can be much thicker than that of a multilayer with the same number of layers but built on a non-porous material. In fact, when polyelectrolytes enter the pores, the thickness of a self-assembled multilayer is not meaningful because it is impossible to accurately measure or clearly define the thickness of the multilayer. This is why, in this work, reproducibility in the separation performance, instead of the thickness, of the composite membranes was studied. The thickness of a self-assembled multilayer over the pores on a porous substrate is very important because these pores are the major or only way of passage for permeation. When the thickness of a self-assembled separating layer over the pores cannot be effectively controlled, the flux and the selectivity of the composite membrane obtained will vary from one membrane to another.

A porous substrate always has a rough surface. The average roughness of a porous PAN membrane is several nanometers (ca. 3-40 nm) [Nguyen et al., 2004]. Different pieces of hydrolyzed porous PAN membranes can have different roughness and this makes it more difficult to obtain a multilayer with repeatable thickness on different points. Thus, it is difficult to obtain the composite membranes with good repeatable dehydration performance.

For composite polyelectrolyte membranes built on a porous substrate with less than 10 self-assembled double layers, the separating layer is very thin and, therefore, very sensitive to defects. Different kinds of defects can exist in a self-assembled composite membrane. Defects can come from the hydrolyzed porous PAN membrane that was used as a substrate to make the composite membranes. For a porous PAN membrane, the pore

size always has a distribution. If there is one pore (defect) on the porous substrate that is too large to be effectively covered by a limited number of depositions, the dehydration performance of the resulting membrane will seriously deviate from its normal value.

Defects could also be formed in a deposition process. If the pores are only partially covered by the polyelectrolyte layers, the resulting membrane is defective. Electrostatic self-assembly, theoretically, has a self-repairing (or self-curing) function and the defects formed in the previous deposition layer may be amended in the subsequent depositions. However, relatively large defects may not be repaired effectively in the fabrication process of the composite polyelectrolyte membranes with less than 10 self-assembled double layers because of limited number of depositions. Even after repair, the local thickness of this repaired spot is different from that of other parts in the membrane, and this will affect the dehydration performance. All defects are formed randomly and cannot be effectively controlled. By using a porous substrate, many uncontrollable factors come into play and these factors certainly affect the reproducibility of membrane performance.

The variation in the thickness of double layers over the pores, random defects on the porous substrate used and the random defects formed in the deposition layers all contribute to the relatively poor reproducibility of composite polyelectrolyte pervaporation membranes, especially for membranes with just few depositions. These defects are inevitable and the low reproducibility of the thickness of a self-assembled multilayer over a porous substrate is also inevitable. Therefore, the relatively poor reproducibility of the composite membranes with few deposited double layers is inevitable.

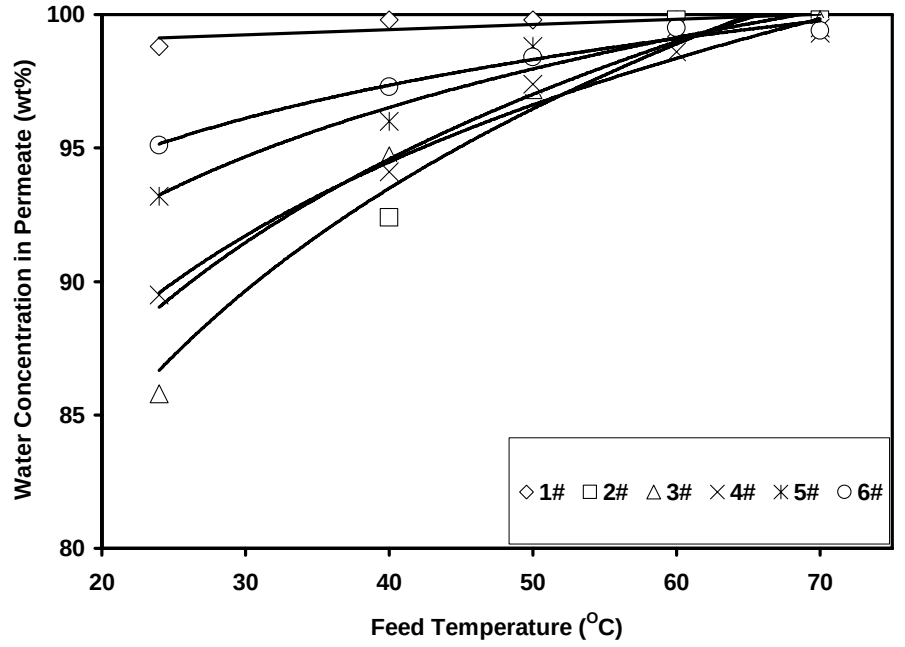
Fortunately, the maximum relative error in the fluxes of the composite membranes with less than 10 self-assembled double layers (shown in Figures 4-2 and 4-3) was about 25%, which is almost the same as the relative error of the thickness of the reported multilayer built on a non-porous substrate [Jiang et al. 2004]. Flux, itself, is an average permeation rate over the membrane surface while the thickness of a deposition layer is an average of few points. When flux is used to study the reproducibility, the

"sensitivity" of the reproducibility has been reduced. This could be the reason why the flux reproducibility of the composite membranes with less than 10 self-assembled double layers was still about 25% even if a porous substrate had been used.

In order to further study the reproducibility of the polyelectrolyte membranes with 7 double layers, 3 additional polyelectrolyte membranes (group 2 membranes, including samples 4, 5 and 6) were prepared under the same conditions as samples 1, 2 and 3. Figure 4-4 is the separation performance of these 6 membrane samples. Tables 4-1 and 4-2 are the separation performance deviations of these 6 membrane samples. Although all 6 membranes (samples 1-6) were made under the same conditions, their separation performance was not identical. The largest relative error in flux between two single membranes could be calculated and it was as high as 25%. Obviously the reproducibility in flux of the composite membranes was not very good.

However if we use the average performance data of several membranes to describe the separation performance of the polyelectrolyte membranes with 7 double layers, the reproducibility is fairly good. Figure 4-5 shows the average separation performance of the composite membranes with 7 double layers, where the number in the legend represents the number of samples used to determine the average performance data. For example, the line 3 in Figure 4-5 is the average performance of sample #1, #2, #3 and the line 5 is the average of #1, #2, #3, #4 and #5.

From Figure 4-5, it can be seen that all averages of the composite membranes obtained are very close. It can be simply proved that the largest relative error between two averages is always smaller than the largest relative error between two single membranes in the same sample population. This means that the separation performance of polyelectrolyte membranes represented by averages is closer to the actual performance than that of a single membrane sample. Figure 4-5 shows that the average performance of polyelectrolyte membranes is fairly reproducible. Also because the average from 2 samples is close to that from 6 samples, the average data of 2 samples can be used to characterize the separation performance of the membranes obtained.



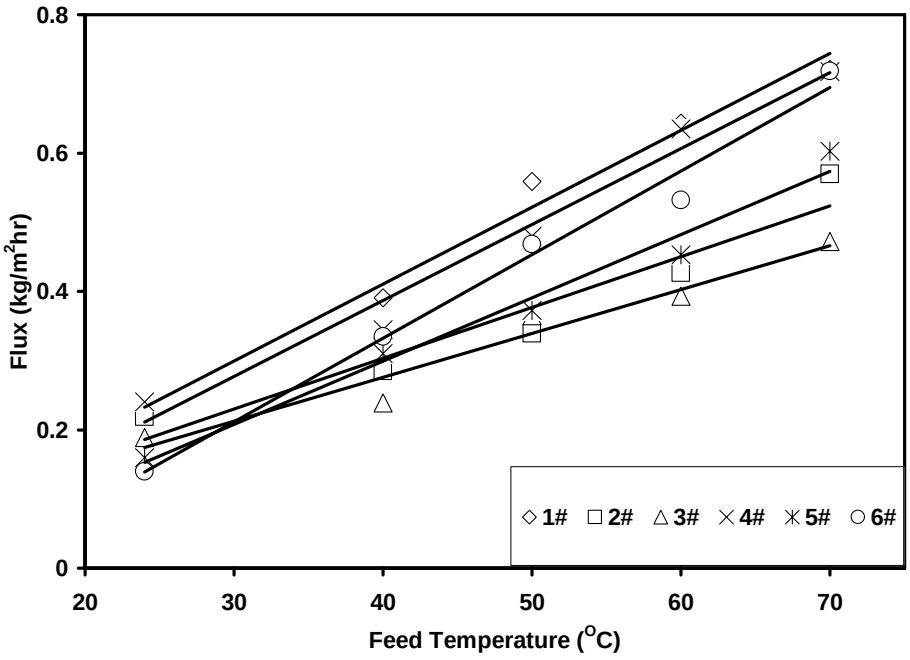




**Figure 4-4. The separation performance of 6 composite membrane samples (7 double layers)**

**Table 4-1. The flux deviation of 6 membrane samples (7 double layers)**

| Temperature ($^{O}$C) | Mean Flux $\bar{q}$ (kg/m$^2$hr) | Standard deviation(σ) (kg/m$^2$hr) |
|---|---|---|
| 24 | 0.196 | 0.036 |
| 40 | 0.318 | 0.048 |
| 50 | 0.431 | 0.078 |
| 60 | 0.514 | 0.098 |
| 70 | 0.634 | 0.094 |

**Table 4-2. The selectivity deviation of 6 membrane samples (7 double layers)**

| Temperature ($^{O}$C) | Mean water concentration in permeate $\bar{c}$ (wt%) | Standard deviation (σ) (wt%) |
|---|---|---|
| 24 | 91.98 | 4.25 |
| 40 | 95.72 | 2.38 |
| 50 | 98.40 | 0.89 |
| 60 | 99.37 | 0.43 |
| 70 | 99.60 | 0.21 |

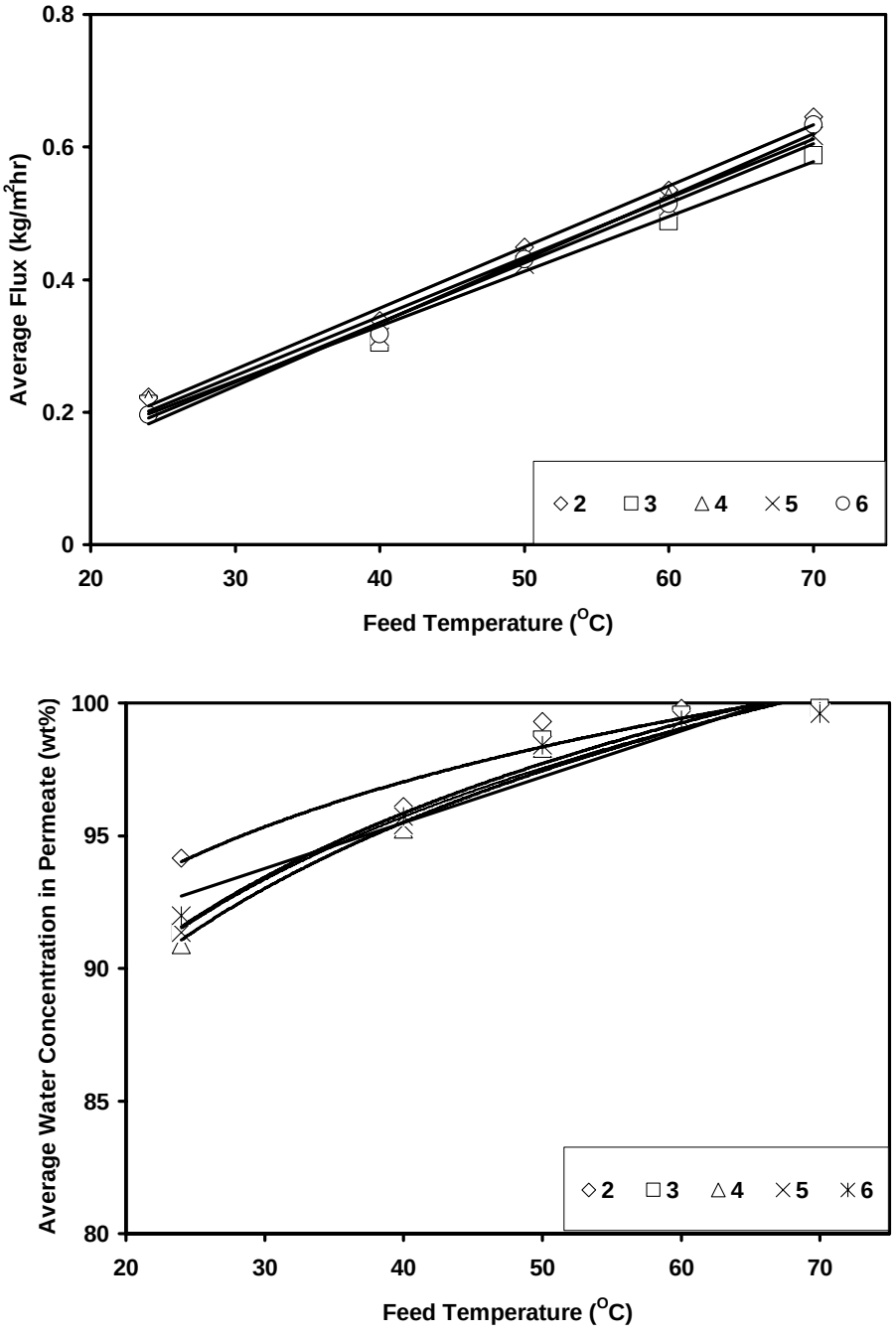



**Figure 4-5. Average separation performance of the membranes with 7 double layers**

### 4.2.2 Separation performance of composite membranes made with different batches of hydrolyzed porous PAN membranes

The dehydration performance of two groups of composite polyelectrolyte membranes made from two different batches of hydrolyzed porous PAN membranes have been tested, and the average fluxes of two membranes from each batch are shown in Figure 4-6. All the composite polyelectrolyte membranes in Figure 4-6 have 7 self-assembled double layers. The average fluxes of two groups of composite polyelectrolyte membranes made from two different batches of hydrolyzed porous PAN membranes are quite different. Two possible reasons can explain these differences.

One is the material difference. Though these two batches of hydrolyzed PAN membranes were made from the same un-hydrolyzed porous PAN membranes, minor differences in structure between different batches still existed. The other is the difference in hydrolysis conditions. It is not possible that the hydrolysis conditions for two batches of hydrolyzed PAN membranes were identical. Different hydrolysis conditions would result in hydrolyzed PAN membranes with different characteristics. When different batches of hydrolyzed porous PAN membranes were used for making the composite polyelectrolyte membranes with the same number of double layers, the dehydration performance of the composite polyelectrolyte membranes obtained would be different.

In order to confirm that the relatively large difference in the average fluxes of the two groups of composite membranes was indeed due to different batches of hydrolyzed porous PAN membranes, two groups of composite membranes that had 2 double layers were fabricated from different batches of hydrolyzed porous PAN membranes, and their separation performance is shown in Figure 4-7. The difference in the separation performance of the composite membranes made from different batches of hydrolyzed porous PAN membranes is still quite obvious. This proves that there is usually a large

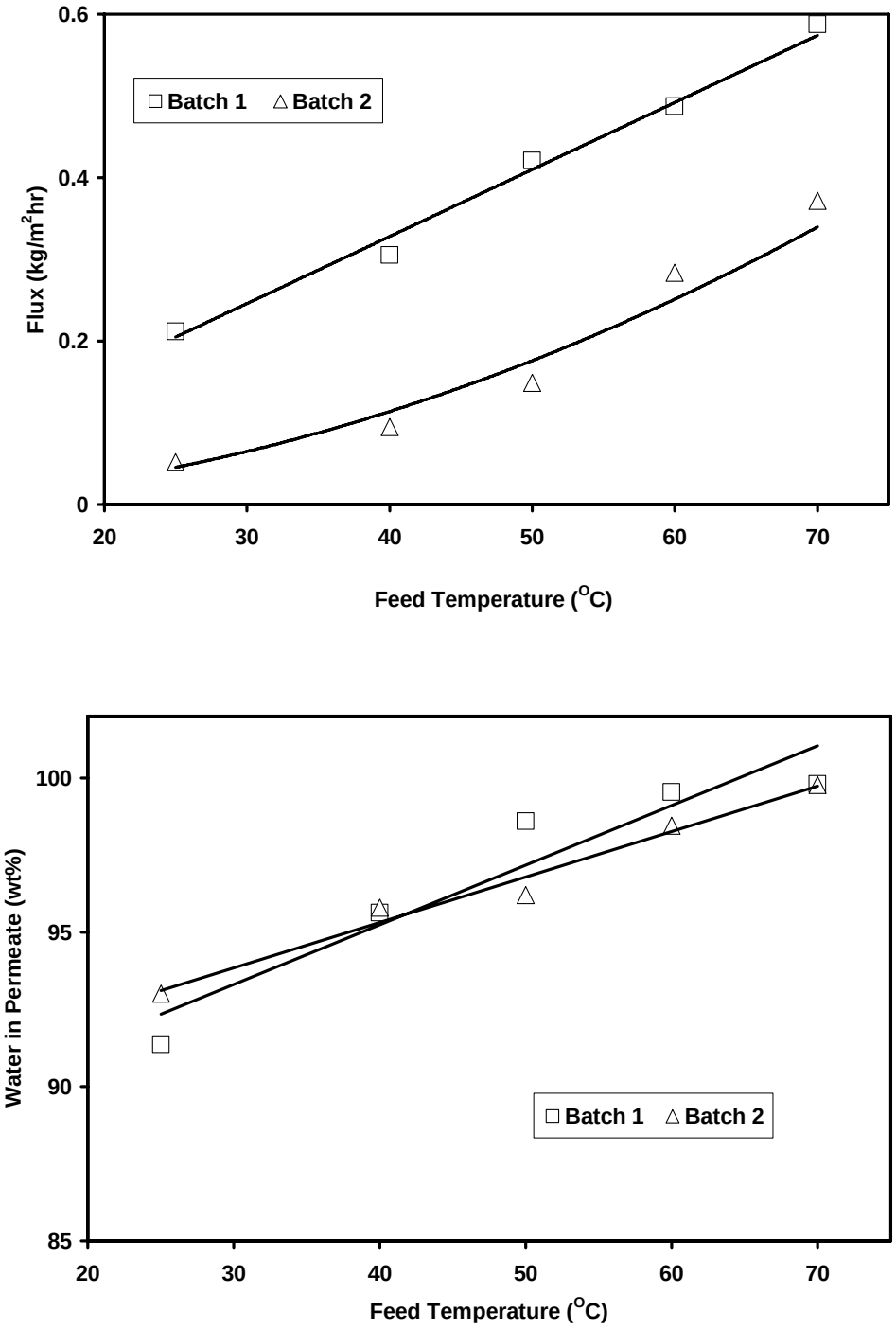



**Figure 4-6. The separation performance of the composite membranes made with different batches of hydrolyzed porous PAN membranes (7 double layers)**

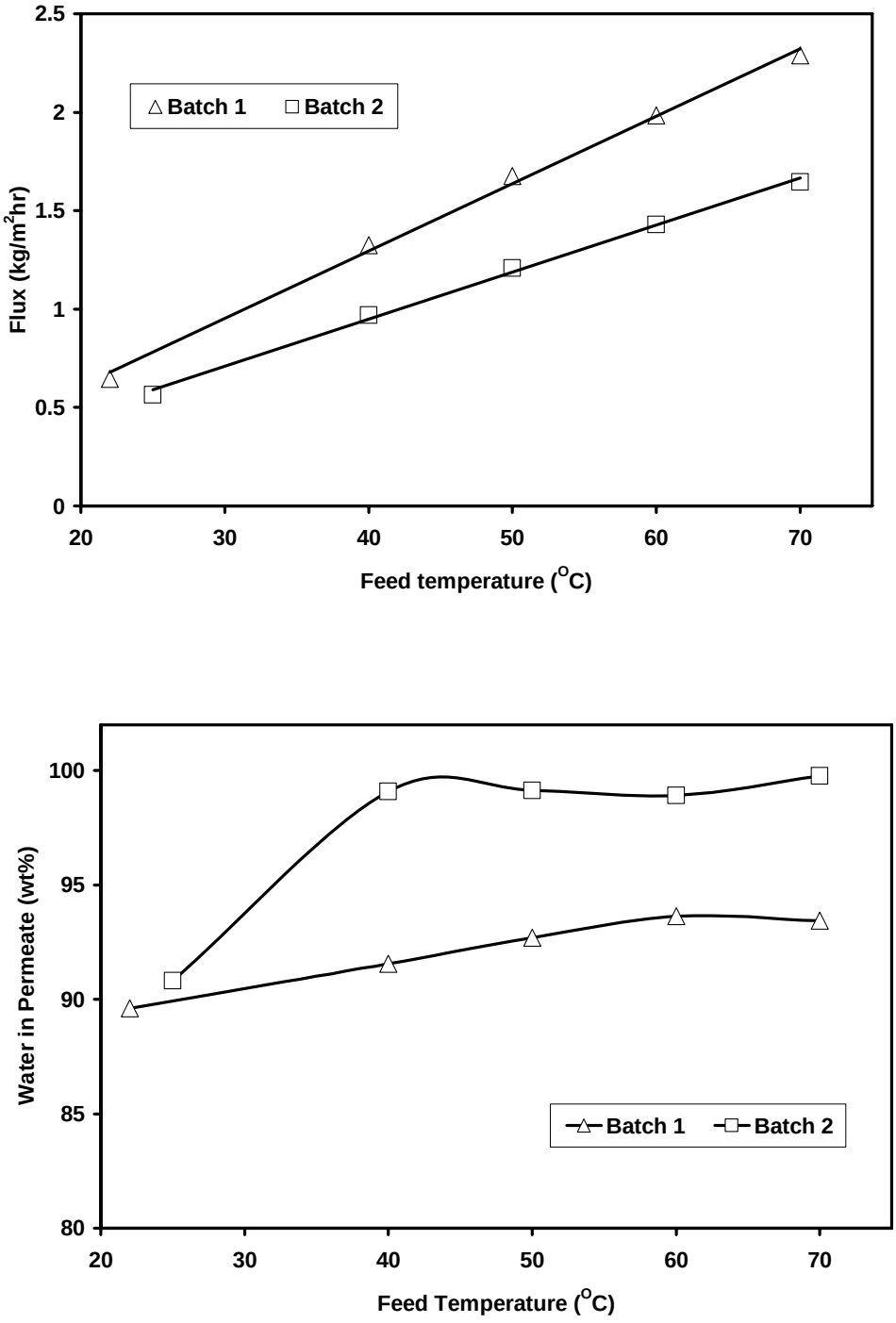



**Figure 4-7. The separation performance of the composite membranes made with different batches of hydrolyzed porous PAN membranes (2 double layers)**

difference in average separation performance of the composite membranes that are made from different batches of hydrolyzed porous PAN substrates.

Using different batches of hydrolyzed porous PAN membranes to make composite membranes introduced one more variable. Though the separation performance reproducibility of the composite membranes represented by the average performance of different membrane samples made from the same batch of hydrolyzed porous PAN membrane was fairly good, the reproducibility of the membranes made from different batches of hydrolyzed porous PAN membranes was poor. It is more reliable to use the same batch of hydrolyzed porous PAN substrate to make membranes for separation performance comparisons.

### 4.2.3 Membrane stability

For the composite polyelectrolyte membranes with less than 10 self-assembled double layers, the fluxes under the same experimental conditions were observed to, more or less, decrease as time passed. The separation performance of a 2-double-layer composite membrane is shown Figure 4-8. At $70^{O}$C, the flux of the composite membrane changed from 1.9 to 1.7 kg/$m^2$hr in 6 hr and this represented a reduction of roughly 10% of the original flux. At $25^{O}$C, the flux of the composite membrane remained constant for 6 hr. The flux reduction of a self-assembled composite membrane seemed to be temperature dependent.

The flux reduction was also found when the pervaporation was conducted in a heating/cooling cycle mode. In the heating process, the feed temperature was increased from room temperature to $70^{O}$C, while in the cooling process, the feed temperature was decreased from $70^{O}$C back to room temperature again. The membrane sample was kept in the feed overnight before the next temperature cycle started next day. Figure 4-9 shows the fluxes of a self-assembled composite membrane with 2 double layers during the heating /cooling cycles. Table 4-3 shows the water concentrations in permeates during the heating/cooling cycles.

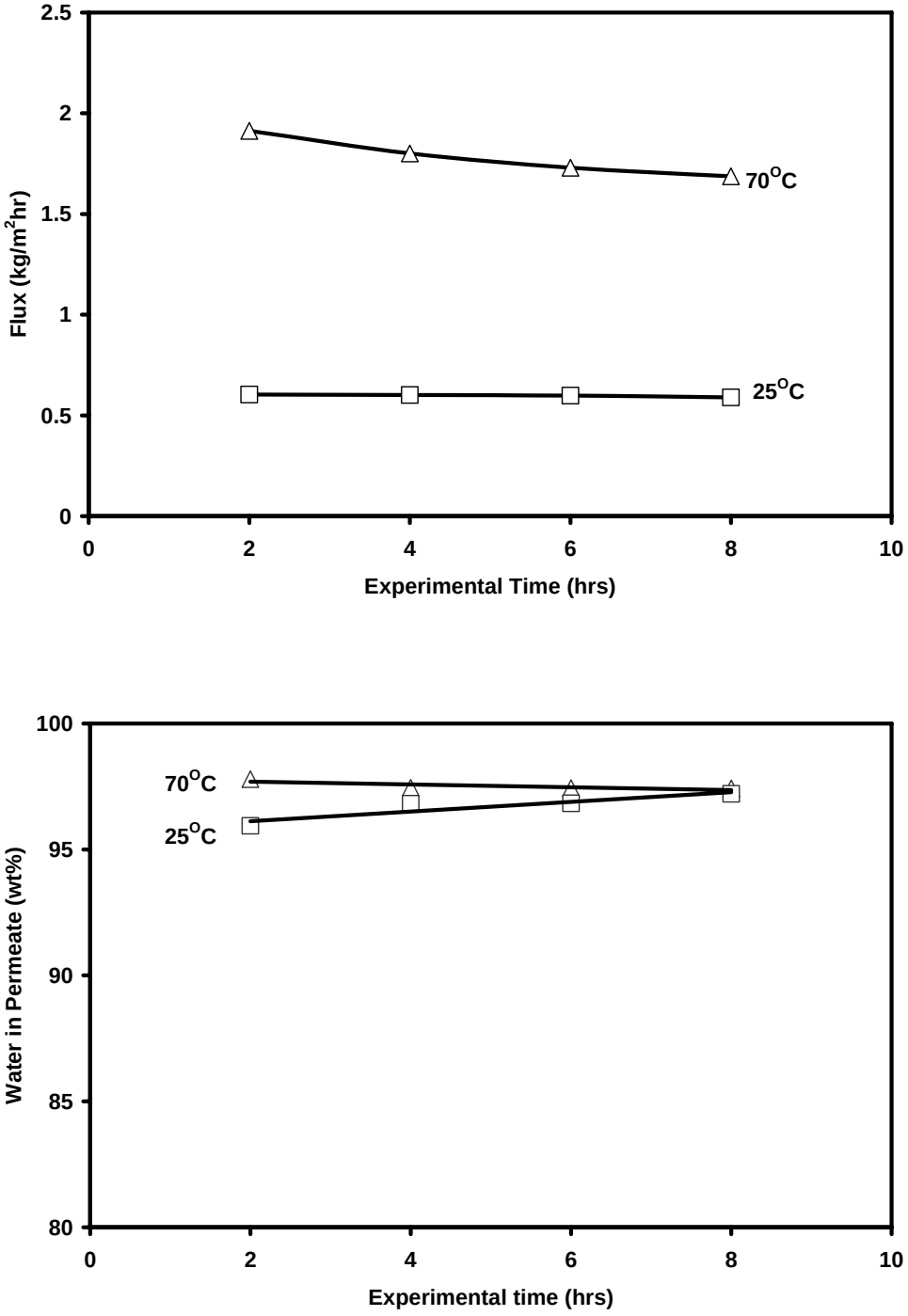



**Figure 4-8. The separation performance of a composite polyelectrolyte membrane with 2 self-assembled double layers at two different temperatures**

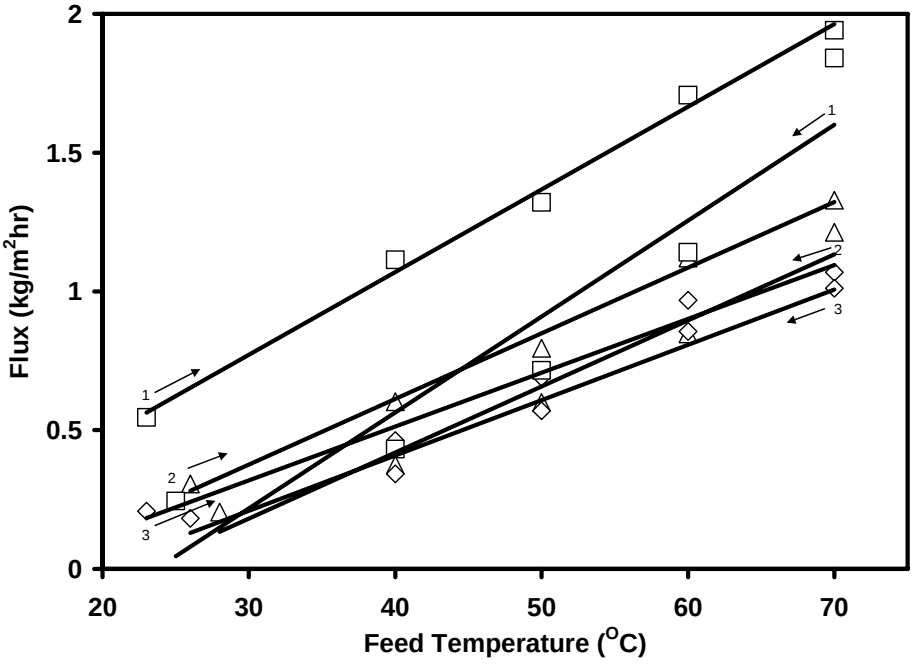



**Figure 4-9. The flux of a composite polyelectrolyte pervaporation membrane with 2 self-assembled double layers during temperature cycles**

□: Cycle 1 Δ: Cycle 2 ◊: Cycle 3

**Table 4-3. The selectivity of a composite membrane with 2 double layers during heating/cooling cycles**

| Temperature (°C) | | | 25 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|---|---|
| Water in permeate (wt%) | Cycle 1 | Heating | 97.6 | 98.1 | 98.4 | 98.4 | 98.4 |
| | | Cooling | 97.4 | 97.4 | 98.2 | 98.4 | 98.6 |
| | Cycle 2 | Heating | 84.9 | 89.6 | 91.5 | 93.1 | 93.3 |
| | | Cooling | 91.6 | 91.8 | 92.0 | 92.1 | 93.6 |
| | Cycle 3 | Heating | 78.5 | 87.0 | 91.2 | 90.4 | 86.9 |
| | | Cooling | 85.3 | 85.6 | 86.1 | 86.3 | 86.7 |

The flux of the composite membrane in a heating process was always higher than that in a subsequent cooling process at the same temperature. This trend was also observed with other composite polyelectrolyte membranes with different numbers of double-layers. Figure 4-10 shows the separation performance of a self-assembled composite membrane that contained 3 double-layers during a heating/cooling cycle. The flux of this composite membrane in the heating process was also higher than that in the cooling process.

Three possible reasons can result in flux reduction in a pervaporation process: the change in feed composition, the change in operating temperature (feed temperature) and the change in membrane structure/ morphology. During our pervaporation runs, only a small amount of permeate sample was injected into a GC for composition analysis each time while most of the permeate sample was put back into the feed tank to maintain a constant feed composition. The quantity of the feed mixture was sufficiently large compared with the quantity of permeate taken in a pervaporation experiment, and as a result, the feed composition was considered to be constant. Because we always compared the fluxes of the membrane at the same operating temperature, the temperature was not the reason for the flux reduction discussed here. The change in membrane structure /morphology was the only possible reason for the flux reduction of a composite polyelectrolyte membrane in a pervaporation process.

The flux reduction of polymeric membranes was generally attributed to polymer relaxation [Yeom et al. 1996]. During a heating/cooling cycle, water absorbed by the separating layer in a composite membrane increases the mobility of polyelectrolytes in the separating layer and makes it easier for polyelectrolytes to relax.

Polymer relaxation is a process in which polymer molecules change from an unstable state to a more stable state. Relaxation is usually caused by stresses. Relaxation takes place in both the heating process and the cooling process because there are stresses caused by expansion and contraction in the separating layer in the heating and the cooling process, respectively. The relaxation caused by heating and cooling, however, cannot be

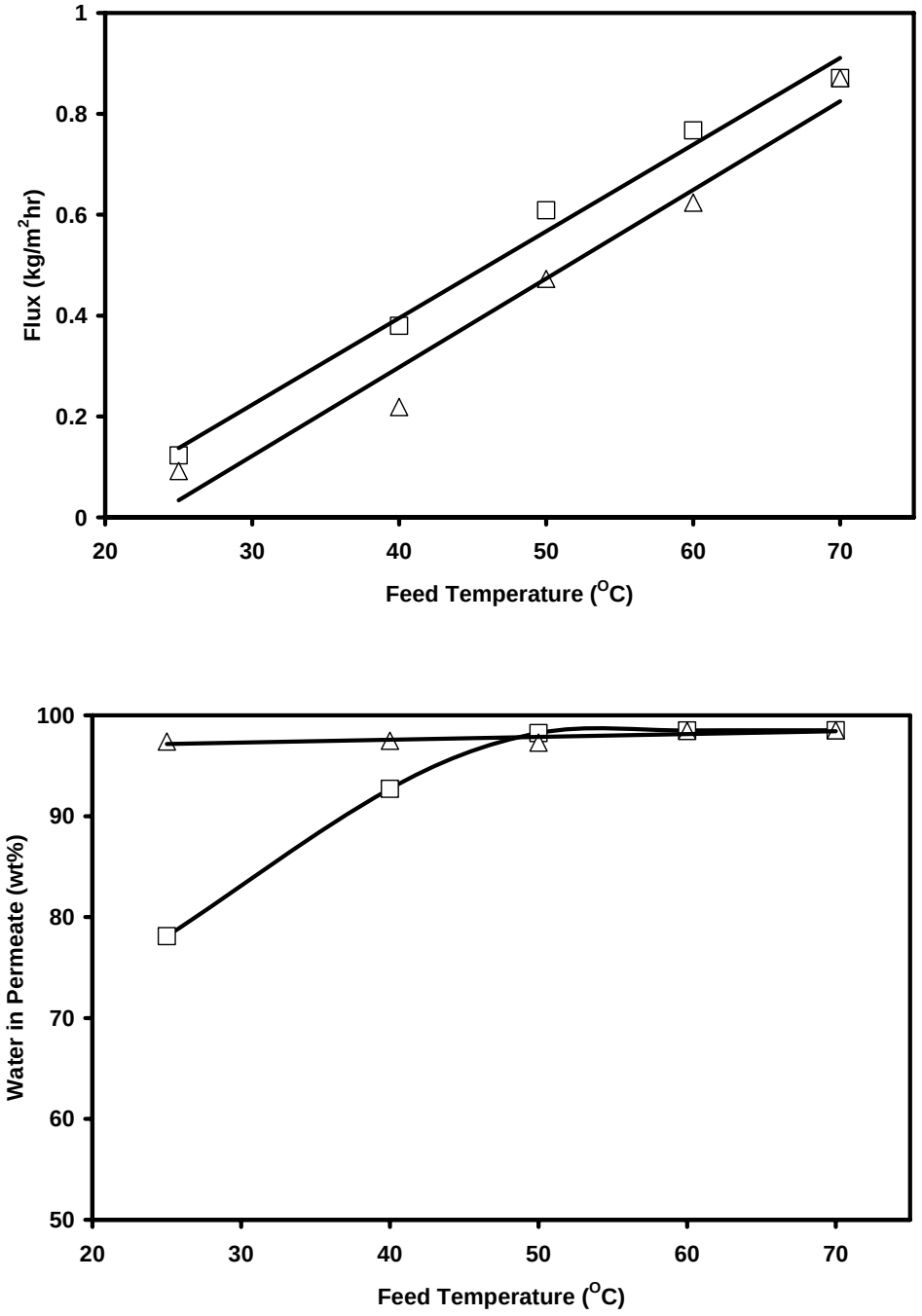



**Figure 4-10. The separation performance of a composite membrane with 3 double layers during a temperature cycle**

□: Heating Δ: Cooling

used to explain why the flux of the composite membrane was always higher in a heating process than in a cooling process at a given temperature. The free volume of a polymer is a function of temperature. In a heating process, the free volume of polyelectrolytes in the separating layer gradually increases, while in a cooling process it gradually decreases. If a polyelectrolyte membrane has been kept at a temperature long enough, the free volume of polyelectrolytes in the separating layer should be the same no matter whether the membrane is cooled down to or heated to the specific temperature. If a polyelectrolyte membrane has not been kept at a specific temperature for a sufficient time, how the membrane reaches this temperature can affect the free volume in the separating layer of the membrane. The free volume in the separating layer in a cooling process, at the same temperature, is larger than or equal to that in a heating process because of the visco-elasticity of the polymer. Thus, the flux of the membrane in a cooling process should be equal to or higher than that of the membrane in a heating process at the same temperature. This does not agree with what we observed in the experiments, which implies that the relaxation alone cannot explain the flux reduction of a self-assembled composite membrane during temperature cycles.

Conformation change may be used to explain the flux differences during the heating/cooling cycles. In a swollen state, the polyelectrolytes can easily change their conformations to yield a thermodynamically more stable and usually denser structure. This process is called densification. Because of the densification, the structure of the self-assembled separating layer becomes more compact and therefore the flux will decrease. The heating process preceded the cooling process in a heating/cooling cycle; the membrane structure in a heating process was less compact than that in the subsequent cooling process. When the membrane structure was less compact, the membrane would have a higher flux. Thus the flux of a composite membrane in a heating process was higher than that in the cooling process at the same temperature. After one heating and cooling cycle, the composite membrane was kept in the feed mixture overnight and the structure of the separating layer became relatively loose because of swelling. The composite membrane might have a higher flux in the heating process of the second cycle than that in the cooling process of the first cycle at the same temperature. Polymer

conformation change is affected by temperature. At a higher temperature, the conformation change takes place more easily and the flux of the composite membrane will decrease with time more significantly. This is why the flux reduction is temperature-dependent, as shown in Figure 4-8. Eventually, the conformations of the polyelectrolytes in the separating layer reach equilibrium, and the flux of the composite membrane will become constant.

Other structure changes can also contribute to the flux reduction of self-assembled composite membranes. Anything that can affect the thickness of the separating layer of a composite polyelectrolyte membrane can affect the flux of the composite membrane. There are various forces acting on a composite membrane during pervaporation, and these forces can, to some extent, change the thickness of the separating layer in the composite membrane. First, there are electrostatic interactions between the inner surfaces of the pores on the substrate and oppositely charged polyelectrolytes in the separating layer built on the porous substrate. Because the inside surfaces of the pores are also charged after hydrolysis and electrostatic interactions will push oppositely charged polyelectrolytes into the pores. Secondly, a very high capillary pressure exists because the sizes of the pores on the substrate are rather small and the surface of the substrate used is highly hydrophilic after hydrolysis. Capillary pressure will also push polyelectrolytes into the pores. Thirdly, vacuum is applied on the backside of the composite membrane during pervaporation, and vacuum also push polyelectrolytes into the pores. According to the solution-diffusion mechanism, one side of the separating layer (vacuum side) is dried while the other side is highly swollen during pervaporation. The polyelectrolyte molecules are rather flexible in a separating layer that is very thin and highly swollen on the feed side. The pairing in an electrostatic self-assembled separating layer is a dynamic process, and this offers a possibility for polyelectrolyte segments or polyelectrolyte chains to move in a pervaporation process. The various forces continuously act on the very flexible polyelectrolyte chains and push them into the pores during pervaporation. The thickness of a polyelectrolyte separating layer over the pores can continuously increase at the beginning of a pervaporation process and then level off. As the thickness of a polyelectrolyte separating layer increases, the permeation flux will

decrease. The thickness change during pervaporation is unique for the composite membrane that has a very fine porous substrate and an ultra-thin self-assembled separating layer. For commercial PVA composite membrane, the thickness of the separating layer will not change with time because the structure of the separating layer is fixed by chemical bonds. In addition to a more compact structure because of conformation change, the increase of the thickness of the separating layer will lead to a more significant reduction in flux.

It is evident that the separation performance of composite polyelectrolyte membranes with less than 10 self-assembled double layers would change with time until a relative steady state was reached.

Figure 4-11 shows the dehydration performance of the composite membrane with 3 double layers in day 1 and after the membrane has been contacted with the feed mixture for 3 weeks. It is shown that the selectivity was improved after 3 weeks (especially at a low temperature), while the flux of the composite membrane was decreased.

Self-assembled composite membranes are expected to have good structural stability. In conventional composite membranes, there is an interface between the separating layer and the supporting substrate. The separating layer and the supporting substrate are usually made from different materials which may behave differently during pervaporation. For example, they may have different degrees of swelling in a feed mixture and delamination, therefore, can easily happen at the interface. In an integral asymmetric membrane, there is no such interface because the skin layer and the substrate are made from the same material. Such a membrane is more stable, but its separation performance is usually not as good as that of a composite membrane. Self-assembled polyelectrolyte composite membranes (current case) offer advantageous features of both membranes. A self-assembled composite membrane is made from two different materials, and the separation performance and the mechanical strength of the membrane can be optimized. In addition, electrostatic interactions keep the separating layer and the supporting layer together. The electrostatic force is much stronger than the van der Waals

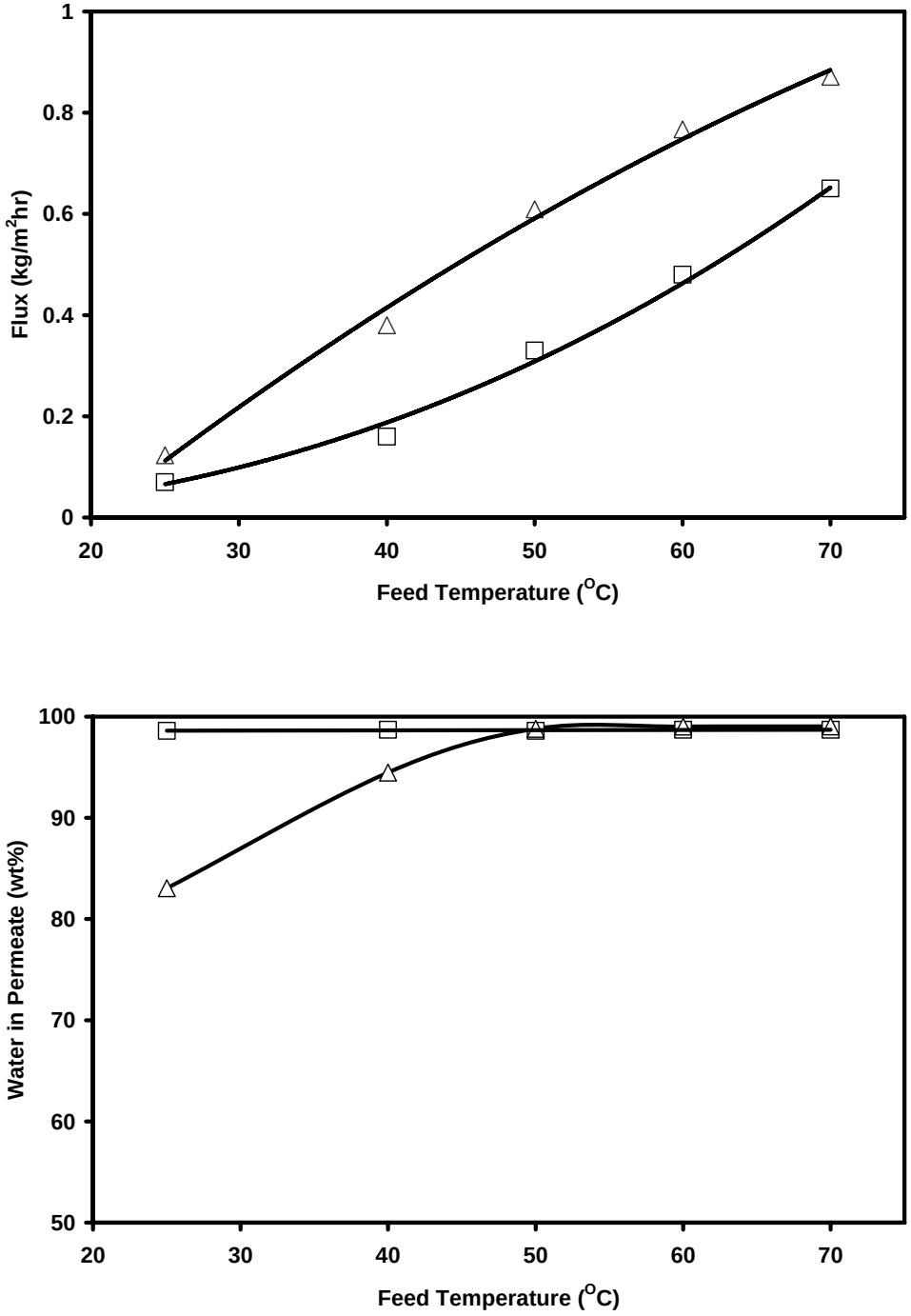



**Figure 4-11. The stability of the composite membranes with 3 double layers**

Δ: Day 1 □: Day 22 .

force, and as such the separating layer and the supporting layer in a self-assembled composite membrane are strongly "bound", leading to good structure stability. This has been supported by Figure 4-11. After 3 weeks, the composite membrane was still highly selective. If the membrane were not stable, the flux of this membrane would increase and the selectivity would decrease. What we see from Figure 4-11 is that the flux of the membrane decreased and the selectivity remained constant. This shows that the self-assembled membrane with less than 10 double layers was stable.

### 4.2.4 Separation performance of composite membranes with different number of self-assembled double layers

Composite polyelectrolyte membranes with different numbers of self-assembled double layers were fabricated and the dehydration performance of these composite polyelectrolyte membranes was determined and compared with each other. Tables 4-4and 4-5 summarize the dehydration performance of these composite membranes. All the membranes used here were made from the same batch of hydrolyzed porous PAN membrane. The data in Tables 4-4 and 4-5 are average of 4 measurements.

From the data in the tables, it can be seen that the dehydration performance of the composite polyelectrolyte membranes with different numbers of self-assembled double layers are different. As the number of double layers in the separating layers increased, the fluxes of the composite membranes decreased (Table 4-4) while water concentrations in permeates increased (Table 4-5). The change of the separation performance of these membranes had a general trend. But because only limited numbers of data were used to calculate the average data, some outliers happened in Table 4-4. For instance, the flux of a composite membrane having 5 double layers was expected to be lower than that of a composite membrane having 4 double layers under the same operating conditions ($70^{O}$C, feed water 9 wt%). However, the opposite was observed. Nevertheless, the separation performance of the composite polyelectrolyte membranes with different numbers of

double layers was basically in agreement with the predictions based on the resistance-in-series model.

Composite membranes with less than 10 double layers have been developed using the pre-selected preparation conditions. The average thickness of a 10-double-layer multilayer built on a non-porous substrate is usually less than 0.1 μm. If the average thickness of a 10-double-layer separating layer built on a porous substrate is also less than 0.1 μm, the flux of the self-assembled composite membrane will be 10 times higher than that of a commercial PVA membrane that has a 1 μm separating layer if only the thickness of the separating layer is considered. In fact, a polyelectrolyte self-assembled separating layer is more hydrophilic than a PVA layer, and the flux of the self-assembled composite membrane mentioned above will be, at least, 10 times higher than that of a commercial PVA composite membrane. However, the fluxes of the self-assembled composite membranes obtained were only 2 or 3 times higher than that of a commercial PVA membrane. This implies that the effective thicknesses of the separating layers in the self-assembled composite membranes obtained, at some points, were over 0.1 μm because of the penetration of polyelectrolytes in the pores of the substrates. The penetration of polyelectrolytes in a porous substrate has substantially reduced the permeation flux of a composite membrane built on a porous substrate. Although the selectivities of these composite membranes were good, the permeation fluxes were still much lower than expected.

**Table 4-4. Fluxes of the composite membranes with various number of double layers**

| No. of double layers | Flux ($kg/m^2hr$) | | | | |
|---|---|---|---|---|---|
| | $25^OC$ | $40^OC$ | $50^OC$ | $60^OC$ | $70^OC$ |
| 3 | 0.12 | 0.38 | 0.61 | 0.77 | 0.87 |
| 4 | 0.07 | 0.13 | 0.31 | 0.48 | 0.64 |
| 5 | 0.07 | 0.17 | 0.37 | 0.59 | 0.73 |

**Table 4-5. Water concentration in permeate for membranes with different number of double layers**

| No. of double layers | Water concentration in permeate (wt%) | | | | |
|---|---|---|---|---|---|
| | 25$^{O}$C | 40$^{O}$C | 50$^{O}$C | 60$^{O}$C | 70$^{O}$C |
| 3 | 78.1 | 92.7 | 98.2 | 98.5 | 98.5 |
| 4 | 88.8 | 96.7 | 98.4 | 99.1 | 99.1 |
| 5 | 97.8 | 99.1 | 99.8 | 99.8 | 99.8 |

# 4.3 Summary

Based on the experimental results, the following statements can be made:

Even though the separation performance of composite polyelectrolyte membranes with less than 10 self-assembled double layers varied by 25%, the membrane reproducibility represented by the average performance of a group of composite polyelectrolyte membranes made under the same conditions and from the same batch of hydrolyzed porous PAN membrane was fairly good. Both the variation in the thickness of the separating layer and random defects in the composite membrane are the causes for the relatively poor reproducibility.

All composite membranes with less than 10 self-assembled double layers were shown to be stable. However, the flux of a composite membrane with less than 10 self-

assembled double layers was observed to decrease with time. Polyelectrolyte conformation change, electrostatic interaction, capillary force, vacuum force and vapor pressure all can contribute to the flux reduction of a composite membrane with less than 10 double layers.

Although the composite membranes developed here have fairly good dehydration performance for IPA/water mixtures, the separation performance of the composite membranes is not as good as expected.

# CHAPTER 5

# EFFECTS OF FABRICATION CONDITIONS ON THE SEPARATION PERFORMANCE OF COMPOSITE MEMBRANES*

## 5.1 Objectives

In the previous chapters, preparation conditions have been selected for the fabrication of composite membranes with less than 10 self-assembled polyelectrolyte double layers using porous supporting materials. Composite membranes containing different numbers of double layers were successfully fabricated and the performance of the membranes for dehydration of aqueous IPA solutions was determined. The composite

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membrane that contained only two self-assembled polyelectrolyte double layers showed good separation performance for the dehydration of IPA/water mixtures. The successful development of composite polyelectrolyte membranes with less than 10 double layers makes self-assembled membrane more practical. The separation performance of a composite membrane is determined by the structure and the morphology of the composite membrane while the structure and the morphology of a composite membrane are affected by the conditions of membrane preparation. The membrane preparation conditions directly influence the separation performance of the composite membrane obtained. When preparation conditions were pre-selected, the influence of preparation conditions on the separation performance of the resulting membranes had not been investigated and most of the preparation conditions were selected empirically. In this chapter, the influence of preparation conditions on membrane performance will be studied. Based on experimental results, some important parameters (e.g., hydrolysis conditions, the type and molecular weight of polyelectrolyte, deposition time and temperature, post-treatment time and temperature) involved in the membrane preparation will be identified and appropriate membrane preparation conditions will be suggested. Unless stated otherwise, the materials and the membrane preparation conditions described in Table3-17 will be used for membrane preparation.

# 5.2 Results and discussion

## 5.2.1 Effect of PAN hydrolysis conditions on the separation performance of composite membranes

### 5.2.1.1 Hydrolysis time

Hydrolyzed porous PAN membranes were used as porous substrates to make composite membranes, and the PAN hydrolysis conditions were expected to affect the separation performance of the composite membranes obtained. In this part, porous PAN membranes hydrolyzed at $75^{O}C$ for different periods of time were used to make

composite membranes, and the separation performance of these composite membranes was tested for comparison.

Figure 5-1 shows the effect of the hydrolysis time of the PAN substrate at a hydrolysis temperature of $75^{O}C$ on the separation performance of the composite membranes obtained. It can be seen that there were no big differences in the water concentrations in permeates whether the porous PAN substrates used for making the composite membranes were hydrolyzed for 20 or 30 min. If the substrate was only hydrolyzed for 10 min, the water concentration in permeate would be relatively low. Only a small amount of -CN groups on the surface of a porous PAN membrane would be converted into carboxylic groups in a short period of time, and there were only a small number of charge points on the surface of the substrate for electrostatic interactions. A small amount of polyelectrolytes could be adsorbed onto the charged surface of the porous substrate, which led to a relatively thin separating layer. As a result, the resulting composite membrane had a relatively high flux and a low selectivity.

Hydrolysis can change the pore sizes of porous PAN membranes. Wang [2000], based on scanning electron microscope studies, suggested that the pore size of a porous PAN membrane increased as the hydrolysis time increased. Our gas permeation tests also showed similar results. It should be noted, however, that the pore size mentioned here is the pore size in the dry state. In the wet state, the pore size of a hydrolyzed porous PAN membrane could decrease as hydrolysis proceeded. Yang and Tong [1997] showed that as the degree of hydrolysis of a porous PAN hollow fiber increased, the hydraulic permeation decreased, indicating a decrease in the pore size of the hydrolyzed PAN membrane in the wet state. As the pore size of a hydrolyzed porous PAN membrane changes, the separation performance of the composite membrane made from the hydrolyzed porous PAN substrate will change. Self-assembly deposition takes place in the wet state, and the pore size of a hydrolyzed porous PAN membrane in the wet state is therefore more important to the separation performance of composite polyelectrolyte membranes than the pore size in the dry state. It is easy to explain the results in Figure 5-1 considering the effect of hydrolysis time on the pore size in the wet state. As hydrolysis time increased, more and more polyelectrolyte molecules would form a swollen layer on

the surface of the substrate and inside the pores, and the pore size of the hydrolyzed porous PAN membrane in the wet state would decrease. When the pore size got smaller, it was easier to cover the pores on the porous substrate to obtain good separation performance. Consequently, as the hydrolysis time increased, the flux of the membrane decreased, while the water concentrations in permeate (or the separation selectivity of the membrane) increased.

#### 5.2.1.2 Hydrolysis temperature

Figure 5-2 shows the effect of hydrolysis temperature on the separation performance of the composite membranes whose separating layers consisted of 4 self-assembled double layers.

As hydrolysis temperature increases, the hydrolysis reaction will be faster. At a given hydrolysis time, increasing the hydrolysis temperature will increase the degree of hydrolysis of the porous PAN membrane, which will increase the electrostatic interactions between the surface of a hydrolyzed porous PAN membrane and the polyelectrolytes to be deposited. This, in turn, affects the separation performance of the composite membranes obtained. For a given hydrolysis time, increasing the hydrolysis temperature, theoretically, can increase the membrane selectivity and reduce the permeation flux. Figure 5-2 shows that at a hydrolysis temperature of $70^{O}$C, the selectivity of the composite membranes was relatively low; while at a hydrolysis temperature of $80^{O}$C, the flux of the composite membrane was also relatively low. $75^{O}$C seemed to be an appropriate temperature for the hydrolysis of a porous PAN membrane. When hydrolysis time was 20 min, increasing the hydrolysis temperature from $70^{O}$C to $80^{O}$C would remarkably reduce the fluxes of the composite membranes obtained.

Based on the results shown in Figures 5-1 and 5-2, it was decided to select $75^{O}$C and 20 min as the “baseline” conditions for the hydrolysis of porous PAN membranes. Figures 5-1 and 5-2 also show that the composite polyelectrolyte membranes made with a porous PAN membrane hydrolyzed under the selected conditions had good separation performance.

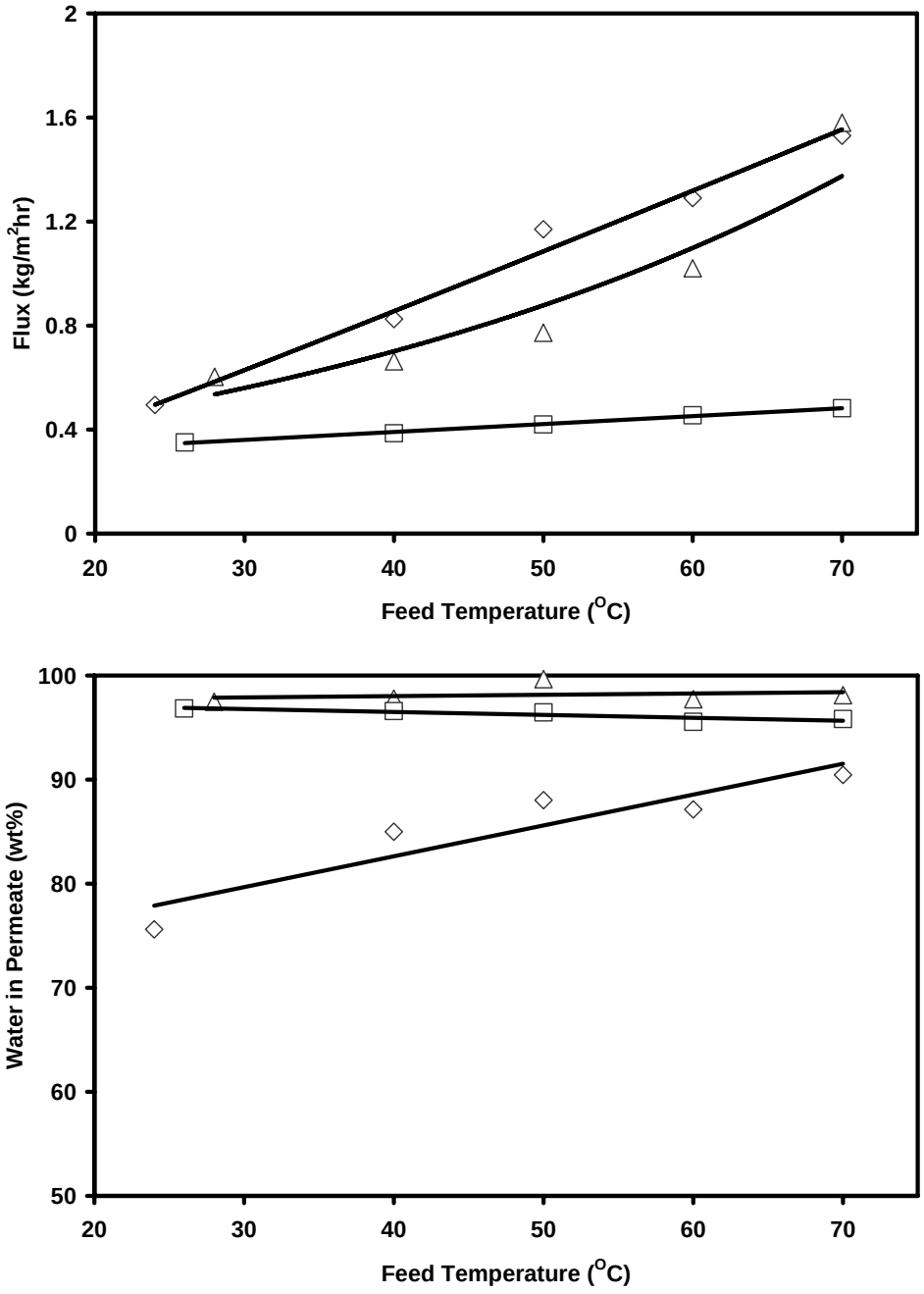



**Figure 5-1. Effect of the hydrolysis time and feed temperature on the separation performance of the composite membranes (3+7 double layers)**

Hydrolysis time: (◊) 10 min, (Δ) 20 min, (□) 30 min.

Hydrolysis temperature: 75°C

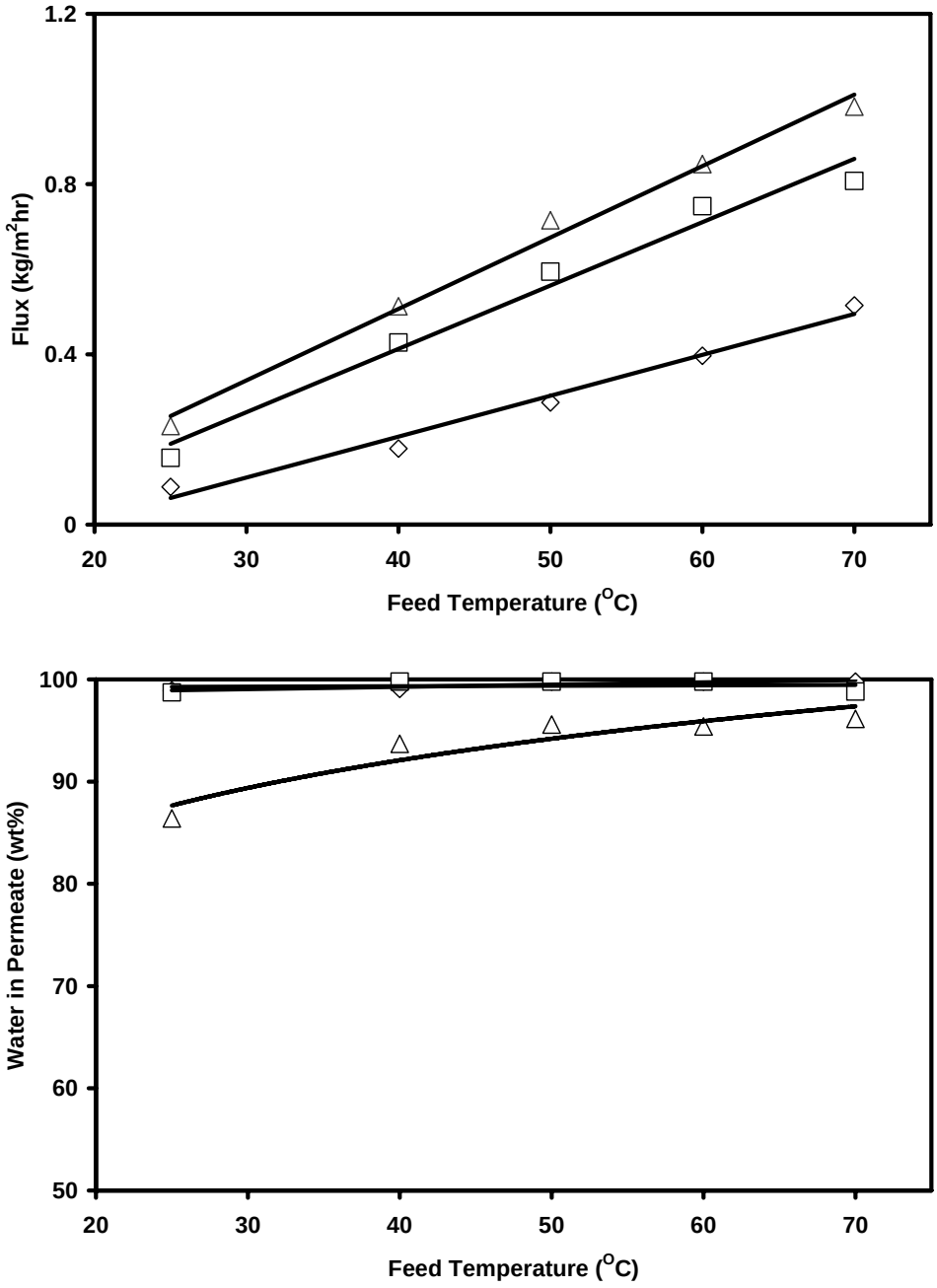



**Figure 5-2. Effect of hydrolysis temperature and feed temperature on the separation performance of self-assembled composite membranes (4 double layers)**

Hydrolysis temperature: (◊) 80$^{O}$C, (□) 75$^{O}$C, (Δ) 70$^{O}$C.

Hydrolysis time: 20 min

## 5.2.2 Effect of polyelectrolytes on the separation performance of composite membranes

### 5.2.2.1 The type of polyelectrolyte

Different polyelectrolytes have different characteristics, and the composite polyelectrolyte membranes made from different polyelectrolytes are expected to have different separation performance. Figure 5-3 shows the effect of the type of polyelectrolyte on the separation performance of obtained composite polyelectrolyte membranes (3+7 double layers, one-sided deposition, poly(acrylic acid) $M_w$ 250,000). It is shown that the composite membrane made with polyethylenimine and poly(acrylic acid) had a much higher selectivity and a lower flux than the composite membrane made with poly(diallyldimethylammonium chloride) and poly(acrylic acid). These two composite polyelectrolyte membranes had the same anionic polyelectrolyte but different cationic polyelectrolytes. Polyethylenimine is a weak polyelectrolyte compared with poly(diallyldimethylammonium chloride), but polyethylenimine has a higher charge density than poly(diallyldimethylammonium chloride). The charge density is defined as the number of ionic groups per number of carbon atom in the repeat unit of a polyelectrolyte complex [Krasemann and Tieke, 2000]. The charge densities of the polyelectrolytes used for electrostatic self-assembly deposition are believed to be especially important. A higher charge density means more electrostatic interaction points on the polyelectrolyte backbone, and a polyelectrolyte complex formed by a high charge density polyelectrolyte pair will have a tight complex network structure that can selectively allow water to go through. Poly(acrylic acid) is a polyelectrolyte with relatively high charge density. The composite membrane made from polyethylenimine and poly(acrylic acid) thus had a high degree of physical cross-linking, which resulted in a low flux and a high selectivity for the dehydration of IPA/water mixtures. On the other hand, the composite membrane made from poly(diallyldimethylammonium chloride) and poly(acrylic acid) had a relatively loose network structure because of the low charge density of poly(diallyldimethylammonium chloride), and the composite membrane

formed from poly(diallyldimethylammonium chloride) and poly(acrylic acid) thus had a high flux but a low selectivity.

From Figure 5-3, it seems that using a strong polyelectrolyte is not a necessary condition to make self-assembled composite membranes with high selectivities. Under some circumstances, the composite membranes made from weak polyelectrolytes can have higher selectivities and lower fluxes than the membranes made from strong polyelectrolytes.

Different from poly(diallyldimethylammonium chloride) that is a strong cationic polyelectrolyte with a low charge density, chitosan is a weak cationic polyelectrolyte with a low charge density. For the sake of comparison, chitosan was also used as a polycation in this work. Different pervaporation membranes made from chitosan have been reported [Nam & Lee, 1997] in the literature, and chitosan has been proved to be a good membrane material for dehydration. It should be of interest to see if chitosan and poly(acrylic acid) are used as a polyelectrolyte pair to make a composite membrane, how the membrane performs for the dehydration of IPA/water mixture. The separation performance of composite membranes made from chitosan and poly(acrylic acid) was compared with that of the composite membrane made from polyethylenimine and poly(acrylic acid), as shown in Figure 5-4.

The charge density of polyethylenimine is higher than that of chitosan, and the composite membrane made from polyethylenimine as a polycation is expected to have a smaller polyelectrolyte complex cavity than the composite membrane made from chitosan as a polycation. As a result, the separation selectivity of the composite membrane made from polyethylenimine as polycation is expected to be higher than that of the composite membrane made from chitosan. Figure 5-4 shows that the composite membrane made from poly(acrylic acid) and polyethylenimine had a much higher selectivity and a lower flux than the composite membrane made from poly(acrylic acid) and chitosan for the dehydration of IPA/water mixtures. The difference in the separation performance of these two membranes demonstrates that the charge densities of the

polyelectrolytes used for making a composite membrane have a significant effect on the separation performance of the composite membranes obtained.

Ideally, a high performance composite membrane should have both a high selectivity and a high flux, but it is sometimes difficult to achieve both. A high performance composite membrane needs to have at least a reasonable selectivity and a reasonable flux. Composite membranes, with either a low selectivity or a low flux, cannot be considered for practical applications.

When a low charge density polycation and a high charge density polyanion were used, the selectivity of the composite membrane obtained was not good enough for practical use for the dehydration of IPA/water mixtures. Only when a high charge density polycation and a high charge density polyanion (e.g. like polyethylenimine and poly(acrylic acid)) were used, the composite membrane obtained was likely to have a high selectivity. Therefore, high charge density polyelectrolytes are preferred for obtaining composite membranes with high selectivities.

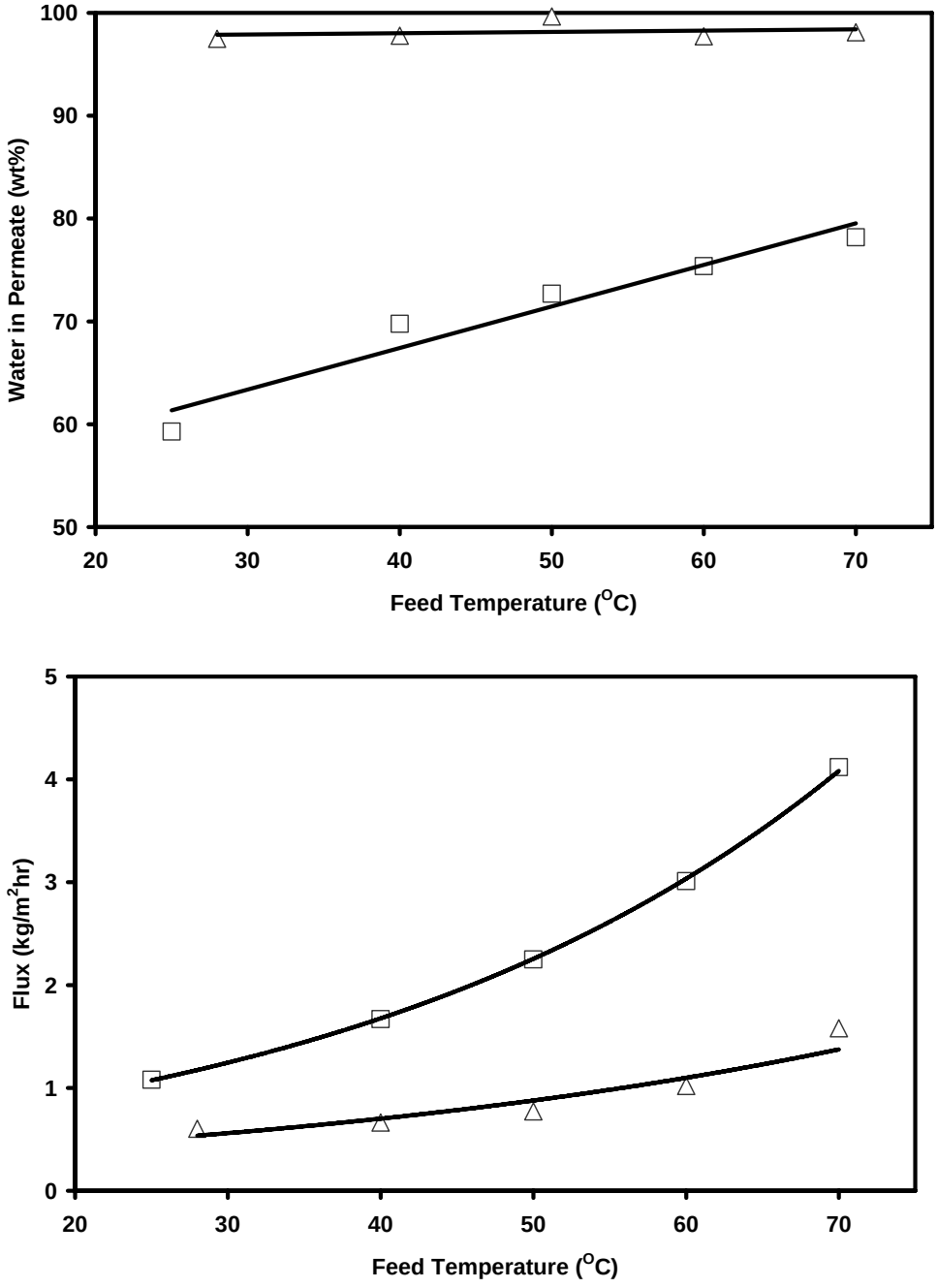



**Figure 5-3. Effect of the type of polycation and feed temperature on the separation performance of the composite polyelectrolyte membranes (3+7 double layers)**

□: Poly(diallyldimethylammonium chloride) + Poly(acrylic acid)

Δ: Polyethylenimine +Poly(acrylic acid)

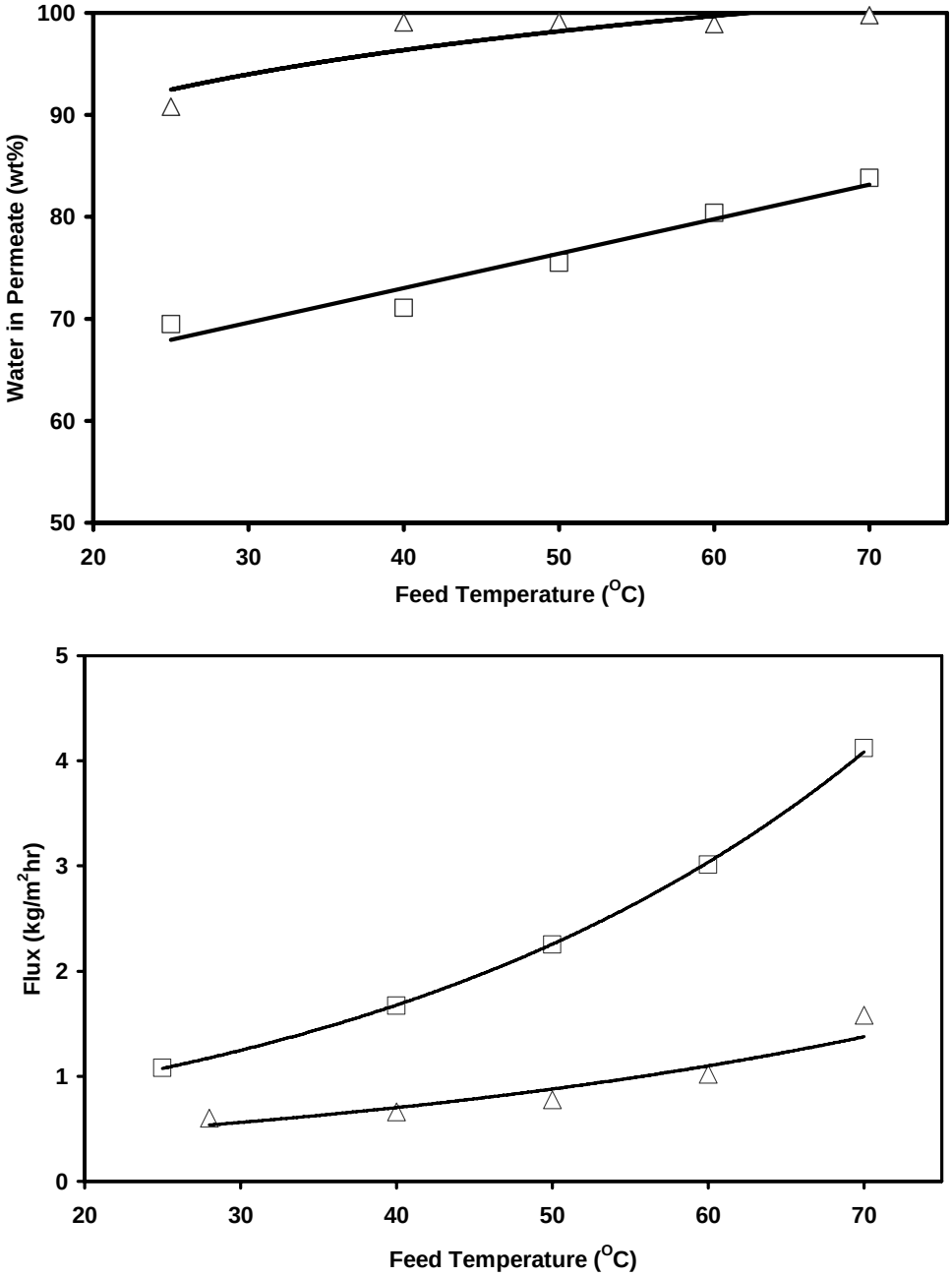



**Figure 5-4. Effect of the type of polyelectrolyte and feed temperature on the separation performance of the composite membranes (2 double layers)**

□: Chitosan+ Poly(acrylic acid) Δ: Polyethylenimine+ Poly(acrylic acid)

#### 5.2.2.2 The molecular weights of the polyelectrolytes

In order to increase the fluxes of composite membranes, porous supporting materials were used in this work. When a porous substrate is used for making a composite membrane using electrostatic self-assembly technique, it is expected that the molecular weight of the polyelectrolyte used will affect the separation performance of the membrane obtained because the molecular weight of the polyelectrolyte will affect the penetration of the polyelectrolyte in the pores of the substrate.

Figure 5-5 shows that a composite membrane made from a high molecular weight poly(acrylic acid) (Mw 1,000,000) had good separation performance. The water concentration in permeate was higher than 98 wt% and the flux was reasonably high. On the other hand, the composite membrane fabricated under the same conditions but made from a moderate molecular weight poly(acrylic acid) (Mw 250,000) had a relatively low water concentration (<70.0%) in permeate and a relatively high flux. There could be some defects in the separating layer of this composite membrane. Increasing the number of self-assembled double layers could "repair" the defects and improve the separation performance. Figure 5-5 suggests that the molecular weights of the polyelectrolytes used significantly affect the number of double layers needed to obtain a defect-free composite membrane. A self-assembled polyelectrolyte separating layer formed by high molecular weight polyelectrolytes would have a better integrity, fewer defects and therefore better overall separation performance. High performance composite polyelectrolyte membranes with less than 10 self-assembled double layers could be fabricated only when high molecular weight polyelectrolytes were used. The use of high molecular weight polyelectrolytes is a prerequisite for making permselective composite membranes with less than 10 double layers.

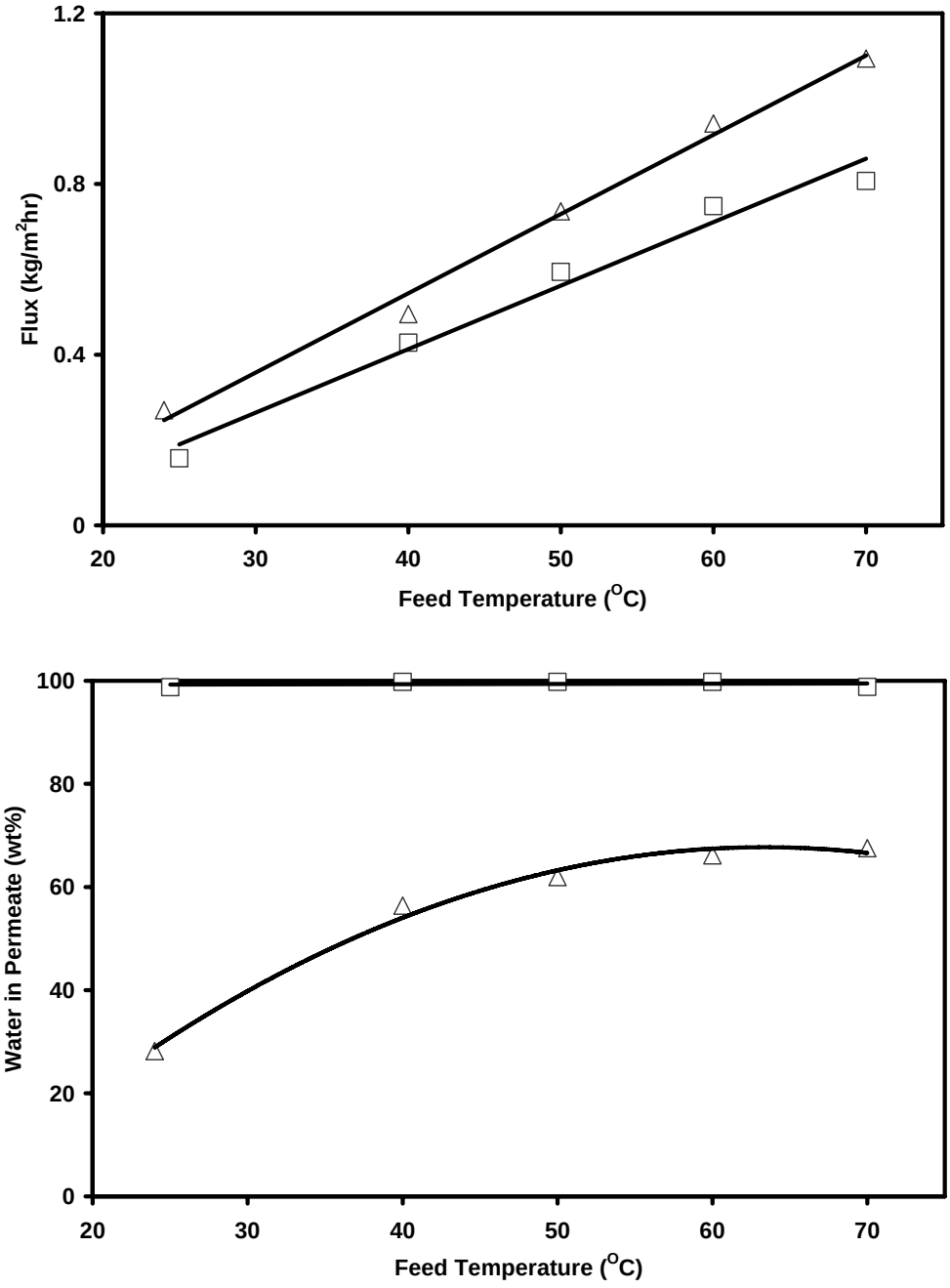



**Figure 5-5. Separation performance of composite membranes fabricated with polyanions having different molecular weights (4 Double layers)**

Δ: Mw 250,000, □: Mw 1,000,000.

## 5.2.3 Effect of fabrication process parameters on the separation performance of composite membranes

### 5.2.3.1 Deposition time

The adsorption of polyelectrolytes on an oppositely charged non-porous surface has been reported to be a two-step process [McAloney and Goh, 1999], i.e., adsorption of polyelectrolytes and then rearrangement of adsorbed polyelectrolytes. This mechanism can be applied for the formation of a self-assembled polyelectrolyte separating layer over a porous substrate if the molecular sizes of the polyelectrolytes are much larger than those of the pores on the substrate.

The adsorption of a polyelectrolyte on an oppositely charged porous substrate is a fast electrostatic interaction. If a polyelectrolyte molecule is in a place close enough to the substrate (which means the electrostatic interaction can happen between the polyelectrolyte molecule and the oppositely charged substrate), the polyelectrolyte molecule will be adsorbed onto the surface of the substrate. After this molecule has been adsorbed, another polyelectrolyte molecule can move in because of the concentration gradient created and then adsorption will occur again. The movement of a polyelectrolyte molecule in the deposition solution near the surface of the substrate, in most cases, is a diffusion process. Diffusion takes time. As a result, more polyelectrolyte molecules will be adsorbed onto the surface of a substrate with time.

In a self-assembled separating layer, defects always exist. If enough time is provided, deposited polyelectrolytes can change their conformations to reduce or repair these defects. Also there are some charges that have not paired with opposite charges in a nascent deposition layer. If enough time is provided, these un-paired charges can get paired through polyelectrolyte conformation changes to form more cross-linking points. The conformation change of deposited polyelectrolytes will reduce defects and improve the separation performance of self-assembled composite membranes. It is possible to change the conformation of a deposited polyelectrolyte chain by post treatment, but it will be relatively difficult because some portions of a specific polyelectrolyte chain may

go into the neighboring layers and interact with the opposite charges in the neighboring layers. Thus the conformation change of a deposited polyelectrolyte chain in post-treatment may need a coordinated movement of polyelectrolytes in several layers. It is much easier to change the conformation of a deposited polyelectrolyte chain when the chain is just deposited. A relatively long deposition time is thus needed to allow the deposited polyelectrolytes to change their conformations and to improve the separation performance of the composite membranes.

Different deposition times have been used in the literature to make polyelectrolyte multilayers with the electrostatic self-assembly technique. The deposition time used by Cheung et al. [1997] to make a polyelectrolyte multilayer on a non-porous substrate was between 2-15 min, while the deposition time used by Tieke et al. [2001] to make a self-assembled polyelectrolyte composite membrane on a porous substrate was over 30 min. The substrate used in this work was porous, and therefore 30 min was pre-selected as the deposition time. An increase in the deposition time could improve the separation performance of obtained composite membranes, but longer deposition time would make the fabrication of a composite membrane more time-consuming. Decreasing the deposition time, from a manufacturing point of view, could make self-assembled composite membranes more feasible.

In Figure 5-6, the possibility of using a deposition time shorter than 30 min is explored. The deposition time was reduced from 30 min to 20 min, and the separation performance of the composite membranes was compared. Changing the deposition time from 30 min to 20 min had little effect on the flux of the composite membrane, but the permeate water concentration was reduced. From a diffusion point of view, a longer deposition time will let more polyelectrolytes diffuse into the vicinity of a charged point on the surface of the substrate, resulting in a higher selectivity. Also, a longer deposition time favors the formation of polyelectrolyte layers with fewer defects because the adsorbed polyelectrolytes have more time to change their conformations to cure the defects in the deposited layer. The data in Figure 5-6 show that a deposition time of 30 min is appropriate for making a composite membrane with good separation performance.

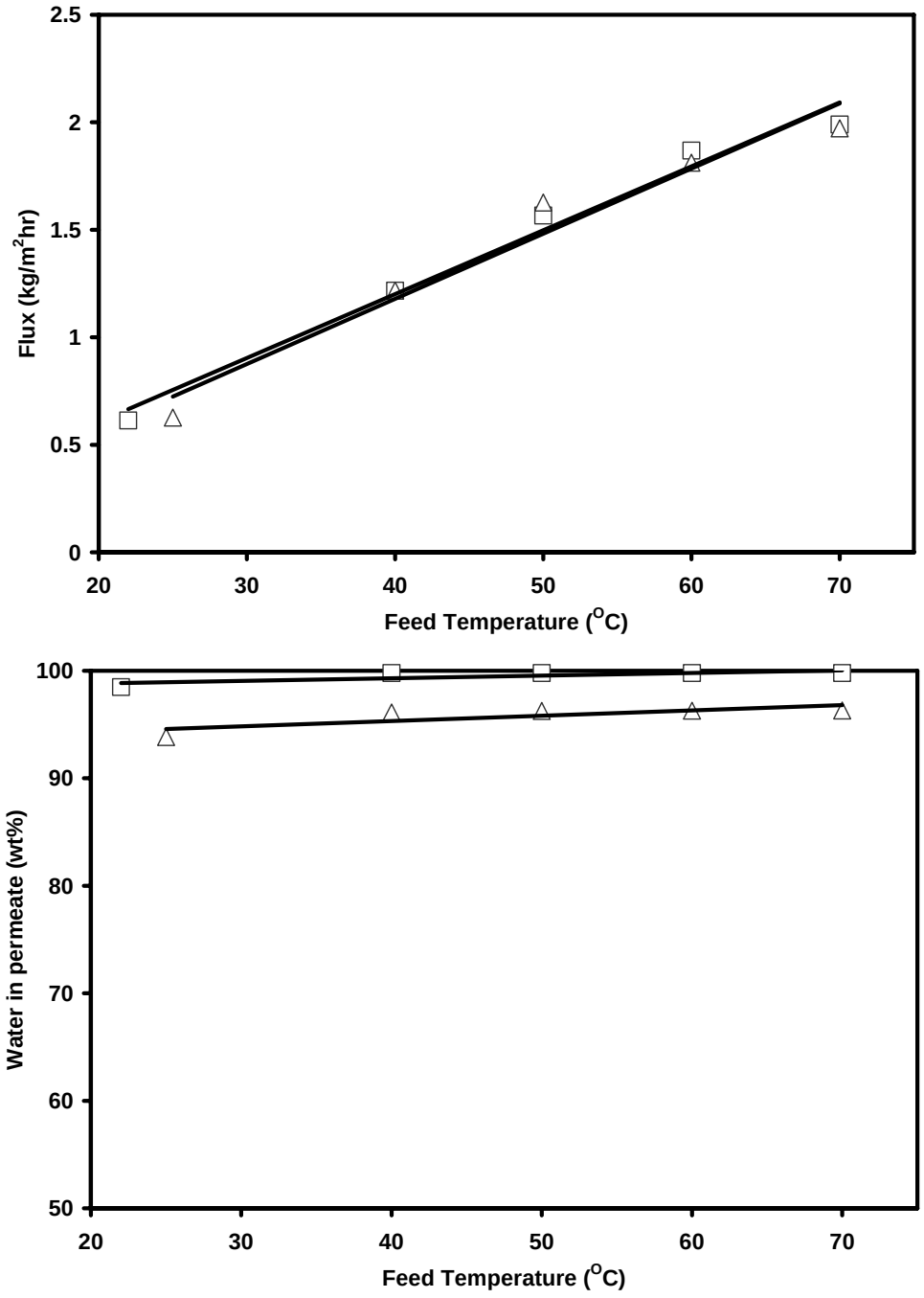



**Figure 5-6. Effect of deposition time on the separation performance of the composite membranes (2 double-layers)**

Deposition time: (□) 30 min, (Δ) 20 min.

#### 5.2.3.2 Deposition temperature

Polyelectrolyte deposition is a diffusion-related process. Increasing the deposition temperature will speed up the diffusion of polyelectrolytes in the deposition solutions and will increase the number of polyelectrolyte molecules to be adsorbed, which will increase the selectivity of the resulting composite membranes. Increasing the deposition temperature also can facilitate the conformation change of adsorbed polyelectrolytes during deposition and thus improve the separation performance further. So increasing the deposition temperature will have a positive effect on the performance of the final membrane. On the other hand, a self-assembled polyelectrolyte deposition process is an entropy-reducing process ($\Delta S<0$) because a polyelectrolyte changes from a random coil to a more ordered layer structure, and it is also an enthalpy-reducing process ($\Delta H<0$) because oppositely charged polyelectrolytes will pair to give off energy. As the self-assembly temperature increases, $|T\Delta S|$ will approach $|\Delta H|$ and the Gibbs free energy of the deposition process thus approaches zero. When the Gibbs free energy of the deposition process is equal to zero, a self-assembly deposition will not take place. It is clear that too high deposition temperature is not favorable for self-assembly deposition. Even in a simple adsorption process, increasing the adsorption temperature will have a negative effect on the adsorption because a simple adsorption also gives off adsorption heat. Therefore, a low temperature will be in favor of the electrostatic self-assembly deposition on the substrate. So, the selection of deposition temperature is critical for the separation performance of the final membranes.

In all reported work about using electrostatic self-assembly techniques to make multilayer structures, most depositions were conducted at room temperature. Considering the diffusion of polyelectrolytes in deposition solutions and the conformation change of the deposited polyelectrolytes, it is desirable to use a relatively high temperature for polyelectrolyte deposition. This is supported by the experimental results. Figure 5-7 shows the separation performance of composite polyelectrolyte membranes with two self-assembled double layers produced at different polyelectrolyte deposition temperatures. It can be seen that as the deposition temperature increased in a certain range, the water

concentration in permeate increased. Polyelectrolytes had higher mobility at a higher temperature, which resulted in a less defective polyelectrolyte separating layer and a higher selectivity. The composite membranes formed at temperatures of 50 and 80$^{O}$C had almost the same fluxes while the composite membrane formed at 25$^{O}$C had a much higher flux. At a lower deposition temperature, fewer polyelectrolytes could be adsorbed in the deposition time used because of the slow diffusion and more defects could be formed in the self-assembled layer due to less conformation changes, which led to a higher flux. The composite membrane formed at 80$^{O}$C had better overall separation performance than the composite membranes formed at 25 and 50$^{O}$C. 80$^{O}$C deposition temperature is therefore recommended for making a composite membrane with less than 10 self-assembled double layers.

Figure 5-7 also justify the necessity of using a modified one-sided deposition method to make self-assembled membranes with less than 10 double layers. If a simple one-sided deposition method was used to make composite membranes, the membranes obtained would have a high flux but a very low selectivity.

Although 80$^{O}$C seemed to be a better deposition temperature than 50$^{O}$C, 50$^{O}$C was still used as the deposition temperature in this work because it was much easier to deposit polyelectrolyte double layers inside an oven at 50$^{O}$C than at 80$^{O}$C. It is too hot to deposit polyelectrolytes at 80$^{O}$C manually.

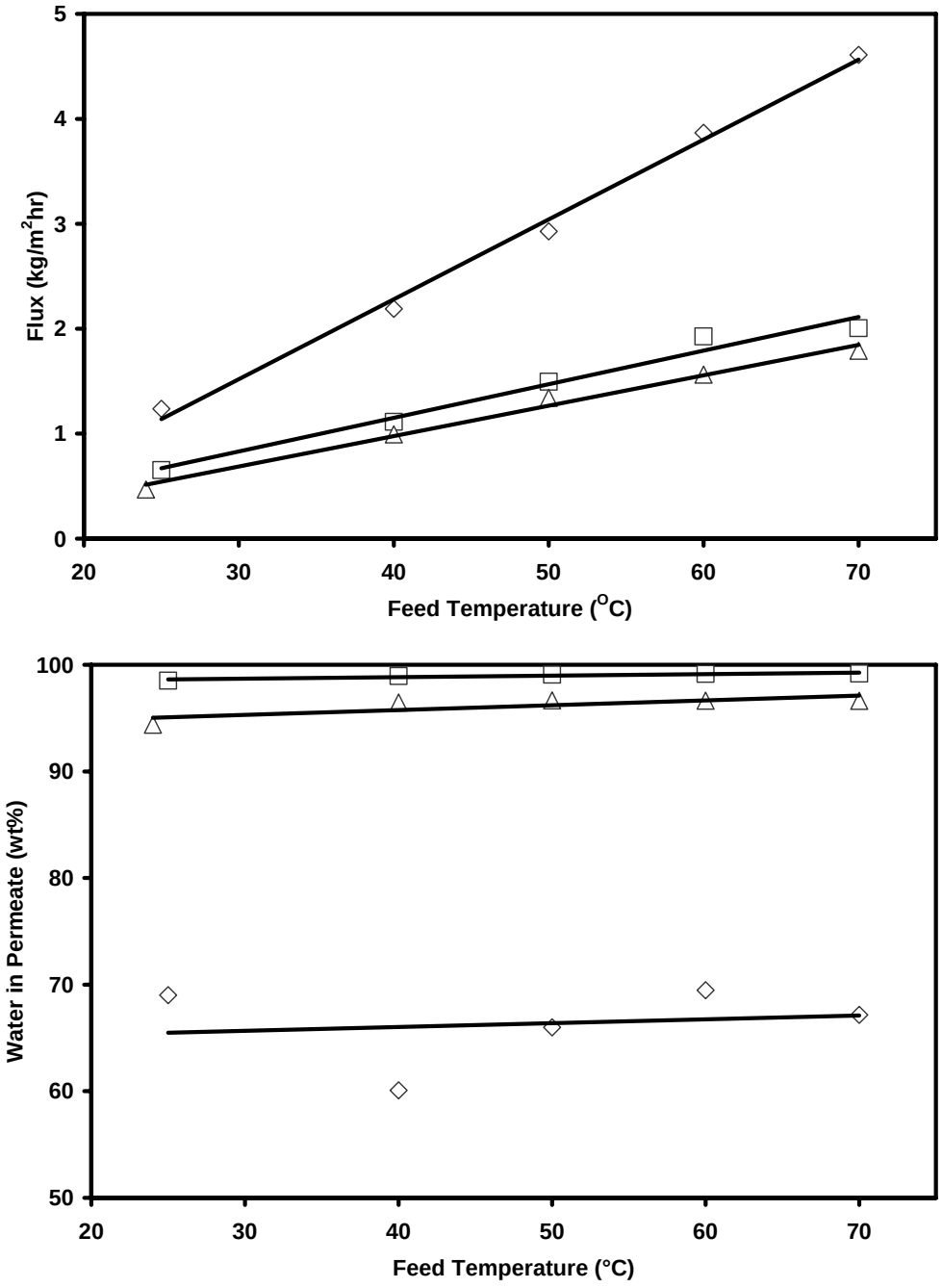



**Figure 5-7. Effect of deposition temperature and feed temperature on the separation performance of the composite membranes with 2 double-layers**

Deposition temperature: (□) 80$^{O}$C, (Δ) 50$^{O}$C, (◊) 25$^{O}$C.

#### 5.2.3.3 Post-treatment time

After multiple depositions, a self-assembled polyelectrolyte separating layer is formed on a porous substrate. The water wet composite membrane is subject to heat-treatment before being used in pervaporation. The post-treatment serves two purposes in this work. One is to dry the membrane sample, and the other one is to change the conformations of deposited polyelectrolytes to improve the separation performance of the composite membrane. Figure 5-8 shows the effect of post-treatment time on the separation performance of a composite membrane with 2 self-assembled double layers. The post-treatment temperature was fixed at $50^{O}C$ for both composite membranes. The separation performance is shown in Figure 5-8 of the two composite membranes post-treated for 12 hr and 1 hr, respectively. The composite membrane post-treated for 12 hr had a higher selectivity and a lower flux. Even though it was difficult for a polyelectrolyte chain in an intermediate layer of a separating layer to change its conformation after the whole multilayer had been formed, it was still possible, to some extent, to change the polyelectrolyte conformation locally should enough time be provided. This kind of conformation change is relatively difficult because this conformation change is a coordinated movement among several segments and even several layers, and sufficient time is hence needed for such conformation changes. As deposited polyelectrolytes change their conformations, the structure of a separating layer will become tight and some defects in the separating layer will be "repaired". Thus, a longer post-treatment time leads to better separation performance.

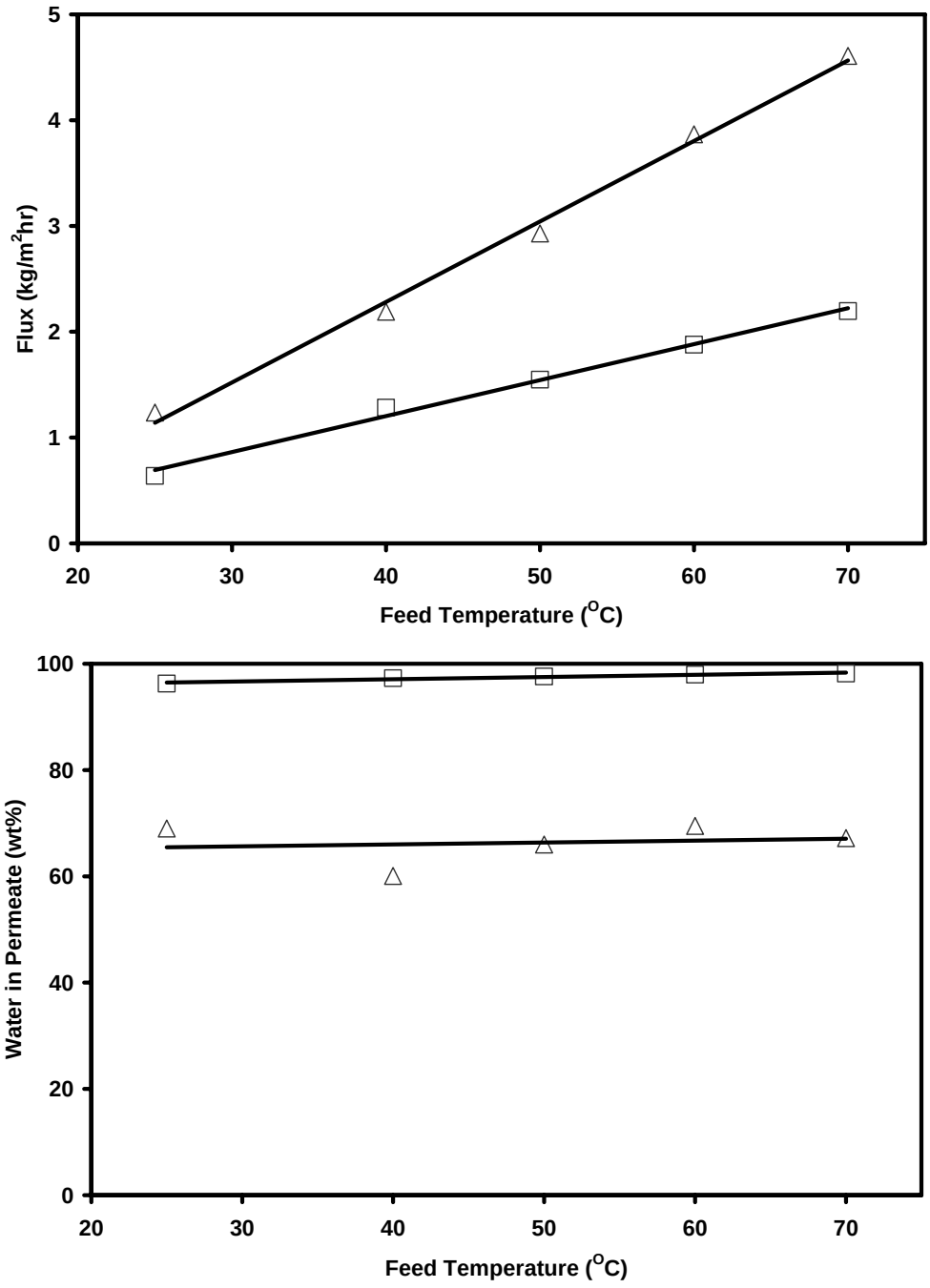



**Figure 5-8. Effect of post-treatment time on the separation performance of the composite membranes with 2 double layers**

Post-treatment time: (□) 12 hr, (Δ) 1 hr.

### 5.2.3.4 Post-treatment temperature

Post-treatment temperature is another variable in a post-treatment process. Post-treatment temperature affects the conformation change of absorbed polyelectrolytes. According to Willams-Landel-Ferry (WLF) equation [He et al. 1990], some phenomena that can be observed in a long time frame at a low temperature can be observed in a short time frame at a high temperature. Using a long post-treatment time and a high post-treatment temperature, some conformation changes that otherwise will not happen can happen, and some defects in the composite membrane will be repaired. This will improve the separation performance of the self-assembled composite membranes.

Figure 5-9 shows the effect of post-treatment temperature on the separation performance of a composite membrane with 3 double layers at post-treatment temperatures of 25 and $50^{O}$C, respectively.

Data in Figure 5-9 show that the composite membrane post-treated at $50^{O}$C had a higher selectivity and a lower flux than the composite membrane post-treated at room temperature ($25^{O}$C). At a higher post-treatment temperature, adsorbed polyelectrolytes had more chance to change their conformations to form additional pairings because of thermal movement. As a result, the composite membrane post-treated at $50^{O}$C would have a tighter polyelectrolyte separating layer than that post-treated at $25^{O}$C. Post-treatment at a relatively high temperature can improve the separation performance of composite membranes. However, if the temperature is too high, the separation performance of the composite membrane will decrease. When the temperature is too high, the evaporation rate of water from a wet membrane will be too fast that some tiny cracks can form because of the stresses. These defects will decrease the selectivity of the membrane. Annealing a self-assembled composite membrane at elevated temperatures was reported by Krasemann et al. [2001]. Annealing can increase the selectivity but it will also reduce the flux of the membrane significantly. The post-treatment process in this work was basically a combination of a drying process and an “annealing” process, and the “annealing” was virtually conducted at a moderate temperature. To obtain a

composite membrane with good separation performance, the post-treatment temperature should be reasonably high. Figure 5-9 shows that $50^{O}C$ is a suitable post-treatment temperature.

#### 5.2.3.5 Dynamic/static deposition process

Two different deposition processes can be distinguished in terms of the movement of deposition solutions: static and dynamic. In a static deposition process, the deposition solution does not move except that the deposition solution in a bottle is shaken for some time at the beginning of the deposition. In a dynamic deposition process, the deposition solution moves all the time. In our research, all depositions were conducted inside an oven. Constant movement of a deposition solution inside an oven required special equipment. A pseudo-dynamic deposition was conducted by shaking the deposition solution every 5 min. This is not a real dynamic deposition, but still sufficient for the effect of the movement of the deposition solution to be observed. Figure 5-10 shows the separation performance of the composite membranes produced using static and dynamic depositions. The composite membrane made with dynamic deposition had a higher selectivity and a slightly lower flux than the composite membrane made with static deposition.

The movement of deposition solutions creates more chances for polyelectrolytes in solution to get close enough to the oppositely charged spots on the surface of the substrate, so more polyelectrolyte molecules can be adsorbed in a dynamic deposition process, which leads to a higher selectivity and a lower flux. However, even in a dynamic deposition process, there still exists a liquid boundary layer near the surface of the substrate and polyelectrolytes still need to diffuse through this layer to reach the substrate surface. Hence factors that affect the diffusion of the polyelectrolytes in solutions will affect the deposition of the polyelectrolytes on the porous substrate and the separation performance of composite membranes. Dynamic deposition is better than static deposition in terms of the separation performance of the membranes obtained. If possible, dynamic deposition should be used for making a composite membrane with less than 10 self-assembled double layers.

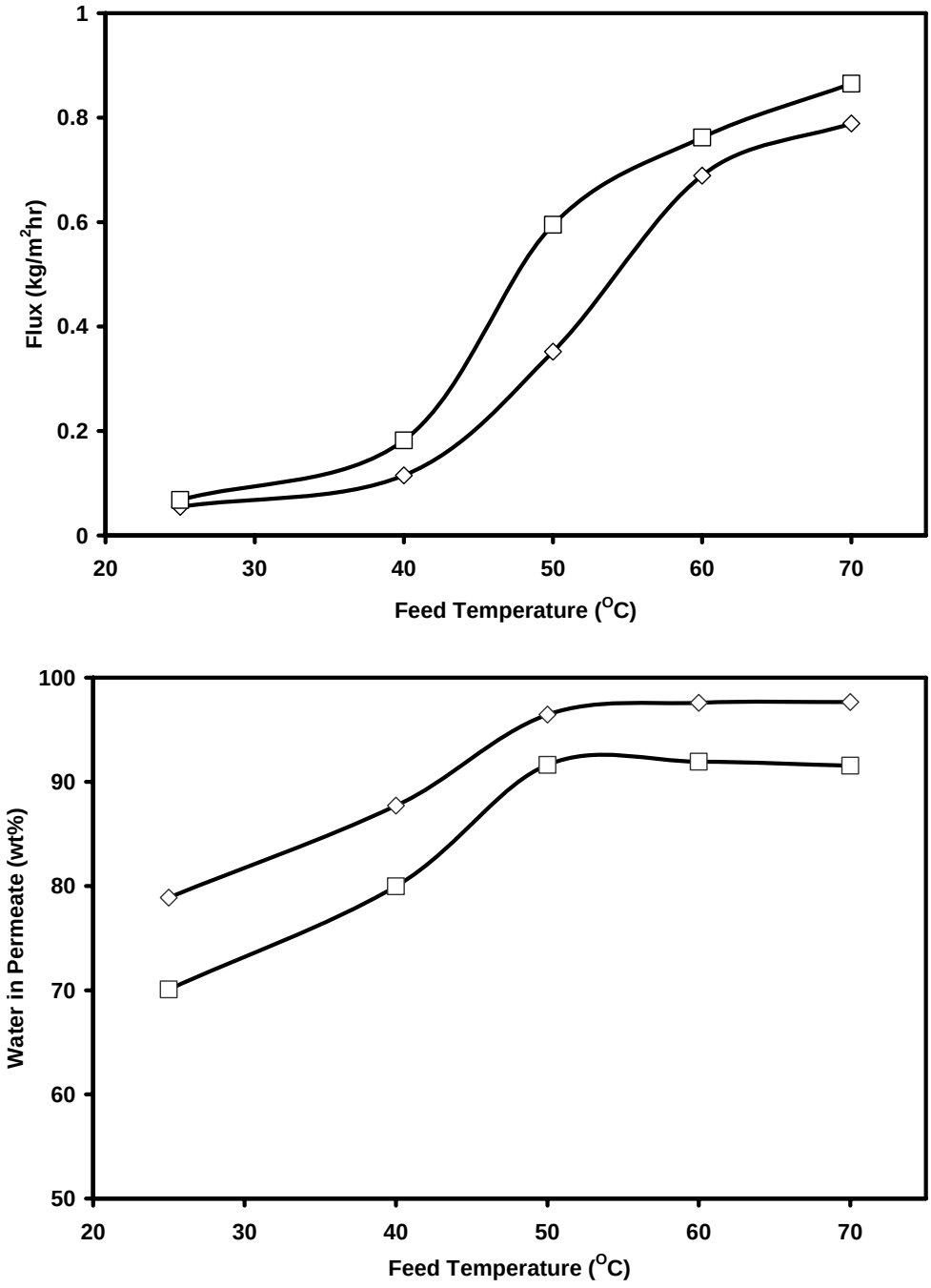



**Figure 5-9. Effect of post-treatment temperature and feed temperature on the separation performance of the composite membranes with 3 double-layers**

Post-treatment temperature: (◊) 50$^{O}$C, (□) 25$^{O}$C.

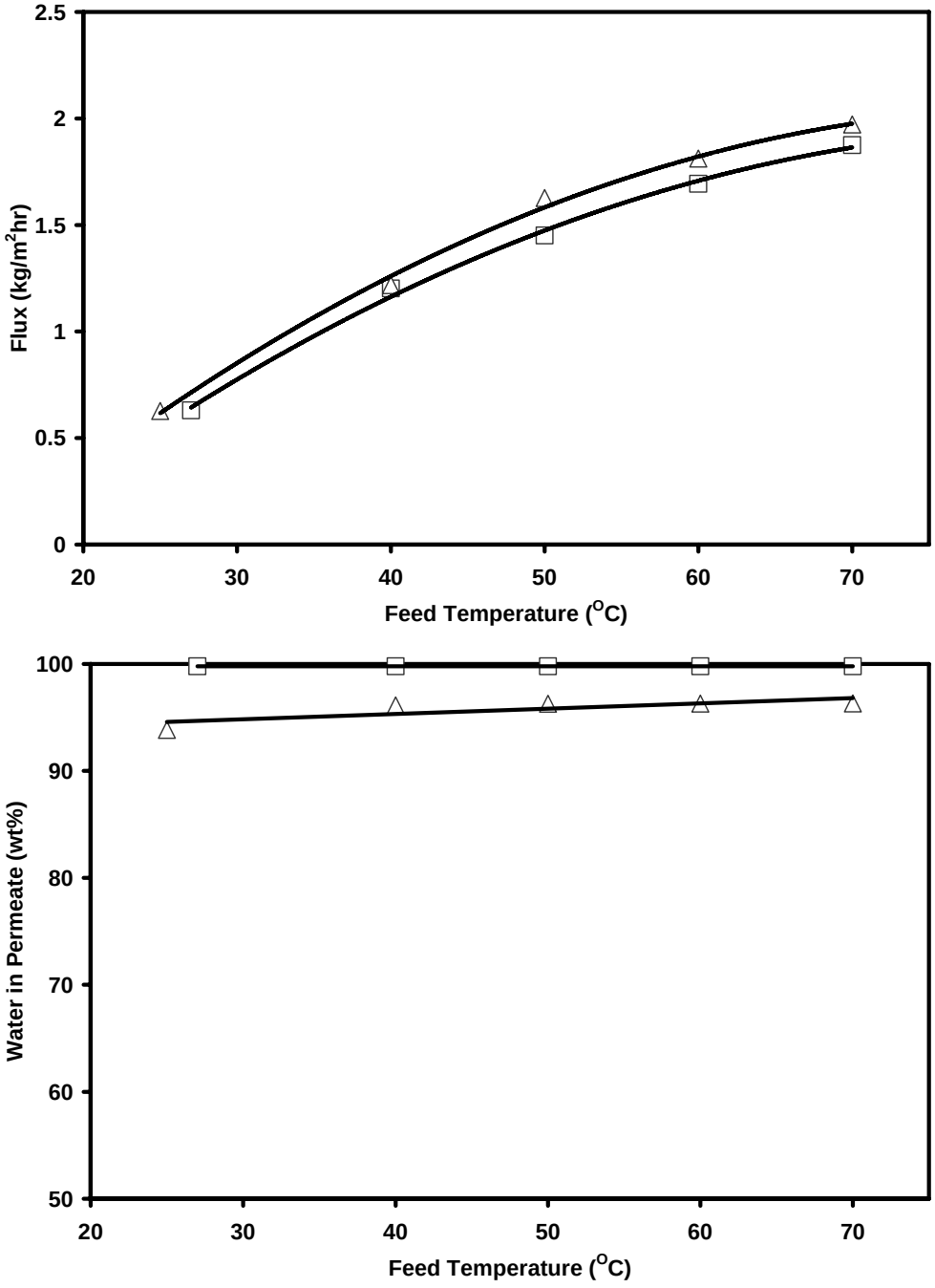



**Figure 5-10. Effect of deposition process and feed temperature on the separation performance of the composite membranes with 2 double layers**

Polyelectrolyte deposition mode: (□) Dynamic, (Δ) Static.

#### 5.2.3.6 Fresh / reused deposition solution

Freshly prepared deposition solutions have been used for the fabrication of the separating layers of the composite membranes we made before. As a comparison, the solutions that had been used previously for making a composite membrane were reused for the fabrication of the separating layer of a composite membrane. Because a solution was used throughout the fabrication of a composite membrane (from the first double layer to the last double layer) in this work, a reused solution might have been used for more than one deposition. If a solution had been used for the fabrication of a membrane (the first membrane) with 2 double layers and if this solution would be used for the fabrication of another membrane (second membrane), this solution was a fresh solution for the first membrane but it was a reused one for the second membrane (this solution had been used twice when making the first membrane). It had not been tried to use the same solution to make the third membrane because of the concern about cross-contamination of deposition solutions. Figure 5-11 shows the effect of solution type on the separation performance of the composite membranes. Figure 5-11 indicates that the membrane made with a fresh deposition solution had a higher selectivity and a lower flux. It is understandable that more polyelectrolyte molecules were in a fresh deposition solution than in a reused solution, and the separating layer of a composite membrane made with a fresh solution tended to have a more compact structure.

Nevertheless, Figure 5-11 also shows that it was possible to reuse the deposition solutions to make composite membranes. Only a small portion of the polyelectrolyte molecules were consumed during each deposition. The consumption of polyelectrolyte in a deposition solution was estimated to be roughly only 1% when a single polyelectrolyte layer was deposited [Schlenoff et al., 2000], which could be smaller than the error of concentration of a solution. For the composite membrane with only two self-assembled double layers, roughly 98% of polyelectrolytes were still in the reused deposition solutions and these solutions could be reused again. Though it was possible to reuse the deposition solutions, fresh solutions were used in preparing the membranes in the work.

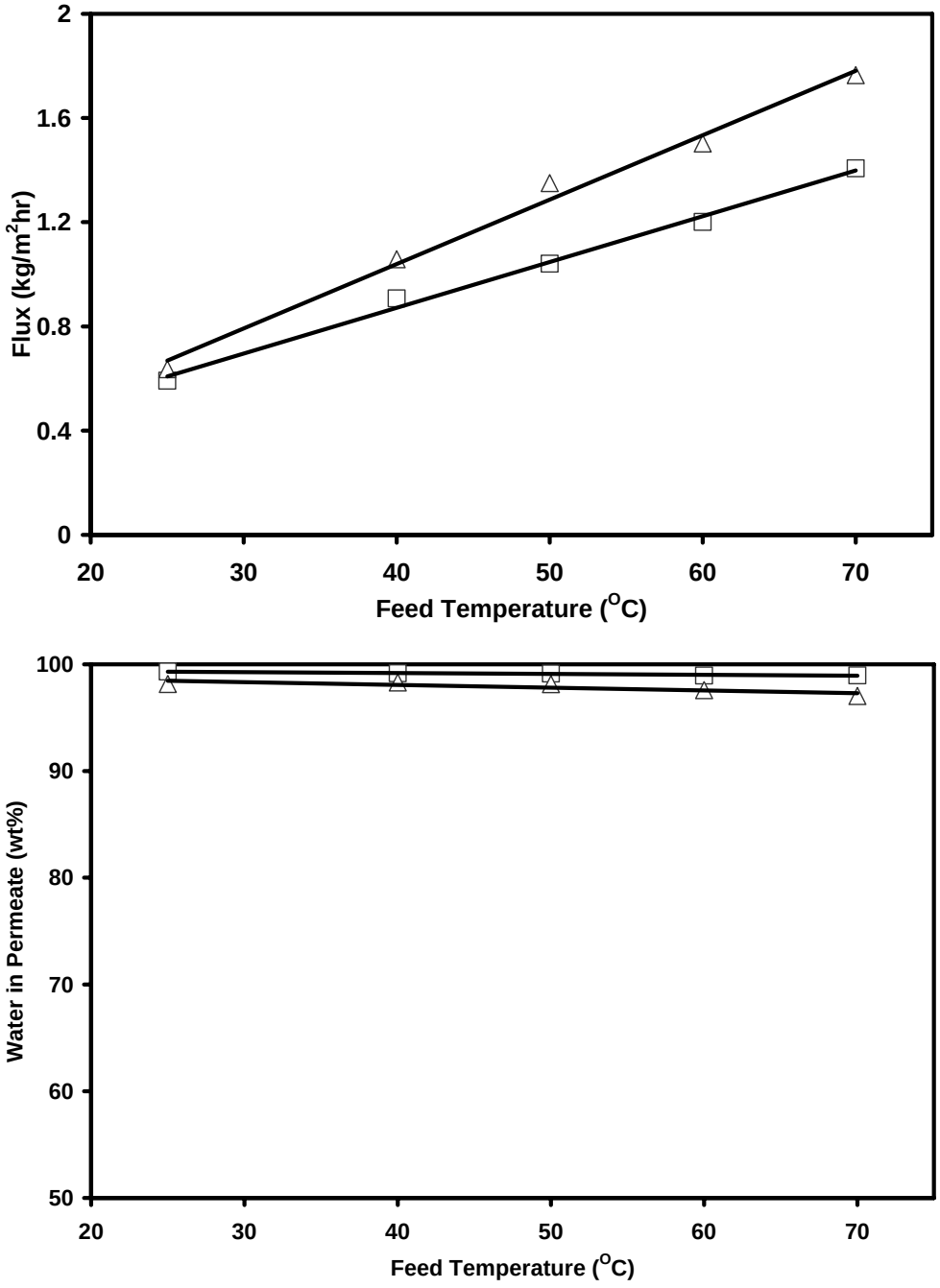



**Figure 5-11. Separation performance of the composite membranes with 2 double layers prepared with fresh/ reused deposition solution**

Deposition Solution: (□) Fresh, (Δ) Re-used.

## 5.2.4 Evaluation of membrane preparation parameters

We have discussed previously the effects of different factors on the separation performance of the composite membranes with less than 10 self-assembled double layers on the basis of one-factor-at-a-time, but the interactions among the factors have not been explored. In this section, the parameter interactions are examined based on the separation performance of the composite membranes. All other fabrication parameters that were not selected as a variable would remain the same as listed in Table 3-17. The number of double layers in the composite membranes used for evaluation of membrane preparation parameters in this study was 2. The purpose was to explore whether there were significant interactions among these factors. If the significant interactions could be found, then the membrane formation conditions could be further optimized.

The fabrication of the composite polyelectrolyte membranes can be divided into three steps: the hydrolysis of a porous PAN membrane to make a charged porous substrate, the deposition on the substrate, and post-treatment of the composite membrane obtained. One major fabrication parameter from each step was chosen as a variable. Table 5-1 shows the factors selected and their levels, and the factorial design is given in Table 5-2.

**Table 5-1. Factors and levels**

| Factor | Level |
|---|---|
| A: Hydrolysis Temperature ($^{O}$C) | 80 (-), 85(+) |
| B: Deposition Time (min) | 15 (-), 30(+) |
| C: Post-treatment Temperature ($^{O}$C) | 50 (-), 75 (+) |

**Table 5-2. Factorial design**

| Experimental Number | Hydrolysis Condition A ($^{O}$C) | Deposition Time B (min) | Post-treatment Temperature C($^{O}$C) |
|---|---|---|---|
| 1 | - | - | - |
| 2 | - | - | + |
| 3 | - | + | - |
| 4 | - | + | + |
| 5 | + | - | - |
| 6 | + | - | + |
| 7 | + | + | - |
| 8 | + | + | + |

The membrane that was made in factorial design experiment number 1 will be designated as membrane number 1. The other membranes are designated accordingly.

The average performance of two composite polyelectrolyte membranes made under the same fabrication conditions were considered the performance of the membranes obtained. The membranes were tested at 5 different temperatures (25, 40, 50, 60 and 70$^{O}$C). The separation performance of the composite membranes fabricated with factorial-design-experiments is given in Table 5-3.

Applying the standard statistics [Duever, 2002], the main effects of these factors and the interactions among these factors have been calculated, and the results are listed in Table 5-4.

Normal probability plots are used to detect the significant effects or interactions. With estimated effects on the water concentration in permeate and on the flux and with the expected normal values, normal probability plots at two different temperatures are obtained (Appendix 13). Figures 5-12 to 5-15 are the normal probability plots of the estimated effects and interactions.

**Table 5-3. The separation performance of the membranes at 25$^{O}$C and 70$^{O}$C (Factorial design)**

| Membrane Number | 25$^{O}$C | | 70$^{O}$C | |
|---|---|---|---|---|
| | Water in Permeate (wt%) | Flux (kg/m$^2$hr) | Water in Permeate (wt%) | Flux (kg/m$^2$hr) |
| 1 | 91.37 | 0.73 | 96.13 | 2.38 |
| 2 | 97.28 | 0.20 | 98.62 | 1.55 |
| 3 | 99.17 | 0.63 | 99.24 | 1.85 |
| 4 | 99.18 | 0.19 | 99.86 | 1.52 |
| 5 | 33.34 | 0.71 | 41.32 | 2.42 |
| 6 | 97.86 | 0.40 | 98.05 | 0.99 |
| 7 | 98.20 | 0.29 | 99.05 | 1.07 |
| 8 | 98.44 | 0.28 | 99.38 | 0.92 |

**Table 5-4. Effects and interactions**

| | | Main Effects | | | 2-Factor Interactions | | | 3-Factor Inter. |
|---|---|---|---|---|---|---|---|---|
| | | A | B | C | AB | AC | BC | ABC |
| 25°C | Water in Permeate | -14.792 | 18.784 | 17.672 | 13.940 | 14.712 | -17.544 | -14.596 |
| | Flux | -0.018 | -0.160 | -0.320 | -0.108 | 0.163 | 0.290 | 0.053 |
| 70°C | Water in Permeate | -14.012 | 15.852 | 15.042 | 13.678 | 13.488 | -14.568 | -13.632 |
| | Flux | -0.475 | -0.495 | -0.685 | -0.215 | -0.105 | -0.445 | 0.195 |

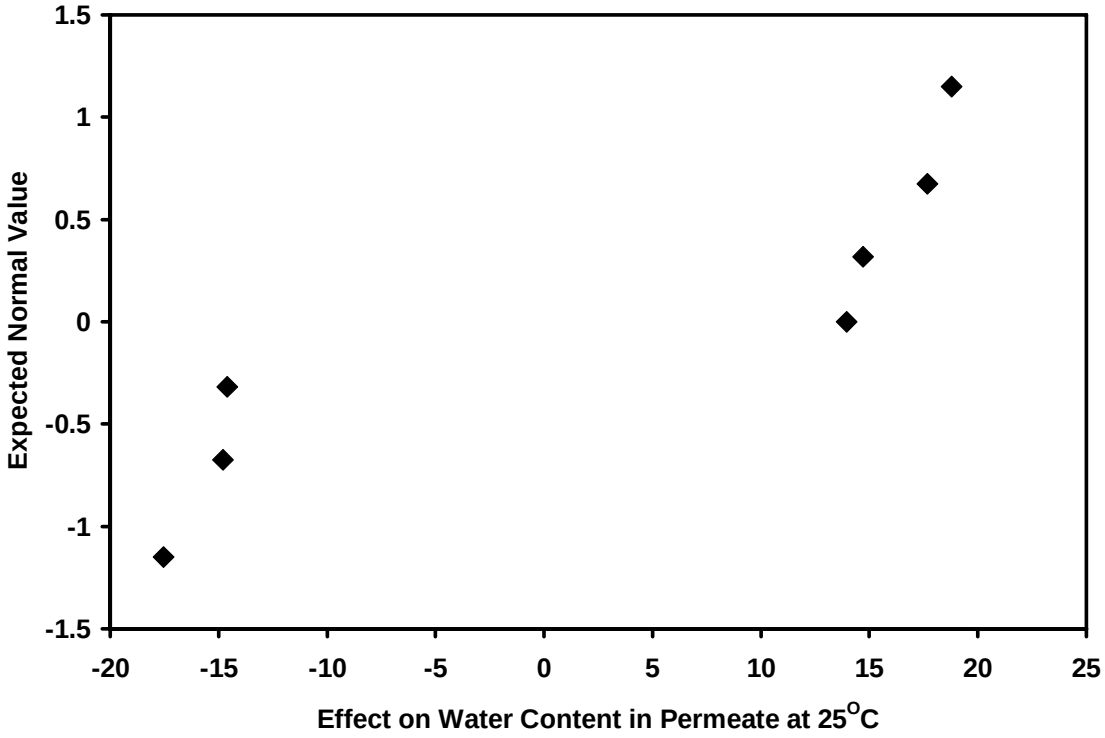



**Figure 5-12. Study of the water concentration in permeate at 25$^{O}$C**

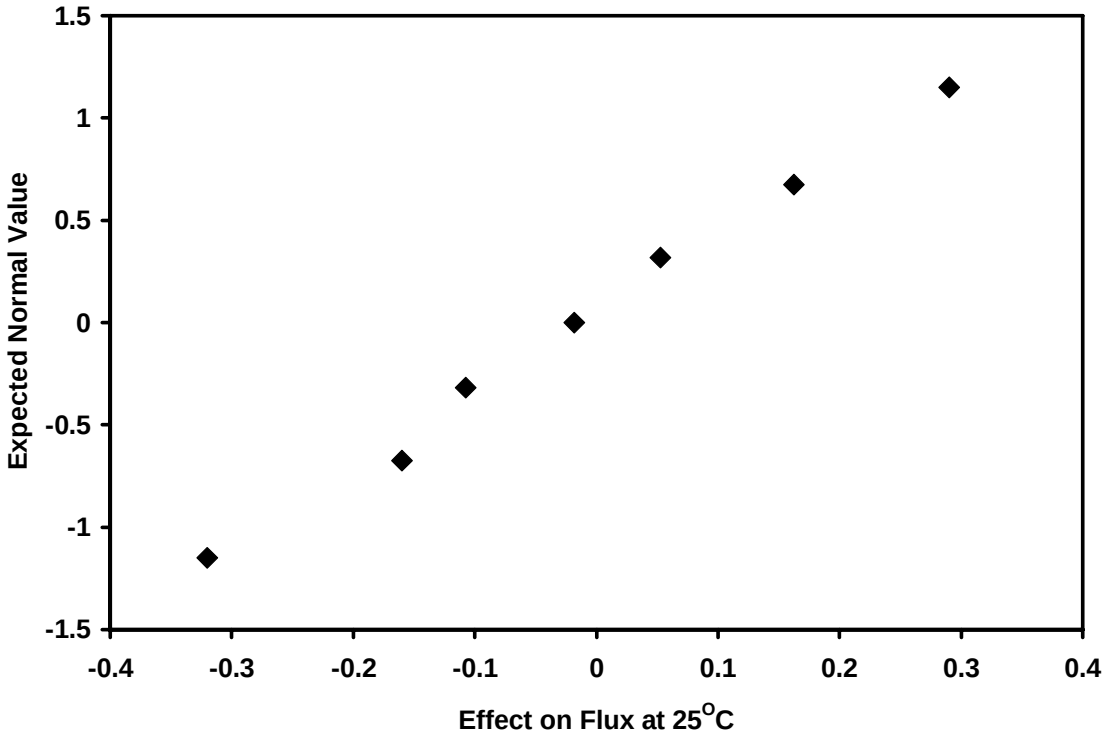



**Figure 5-13. Study of the flux at 25$^{O}$C**

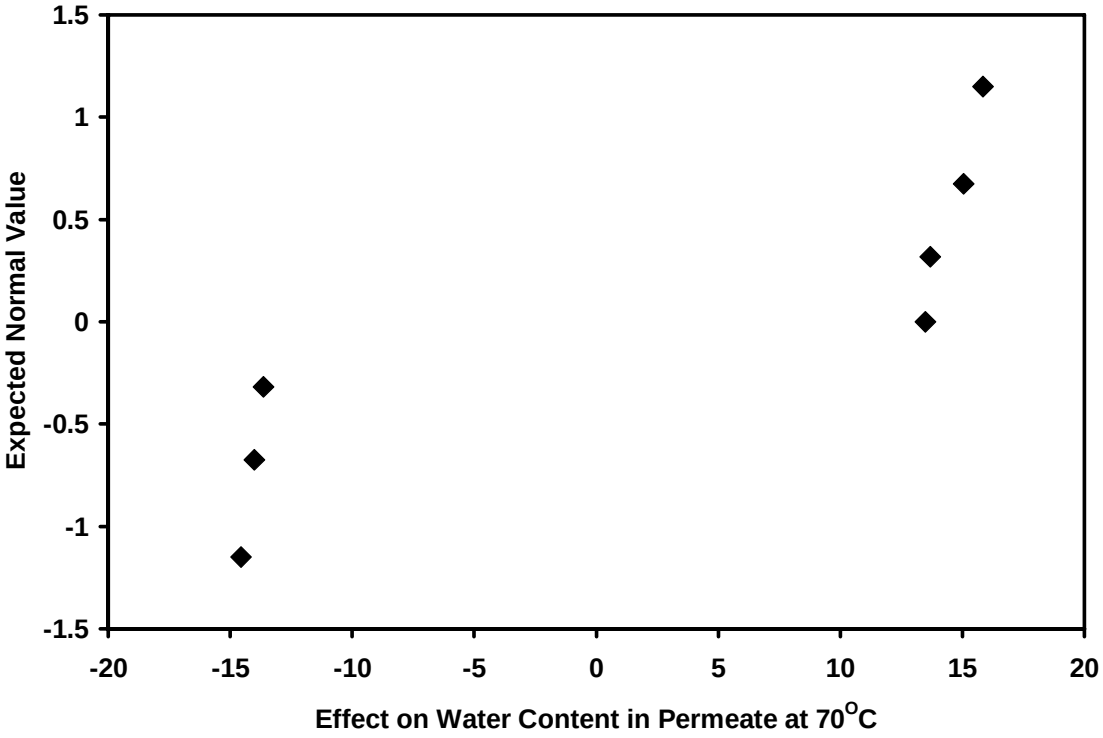



**Figure 5-14. Study of the water concentration in permeate at 70$^{O}$C**

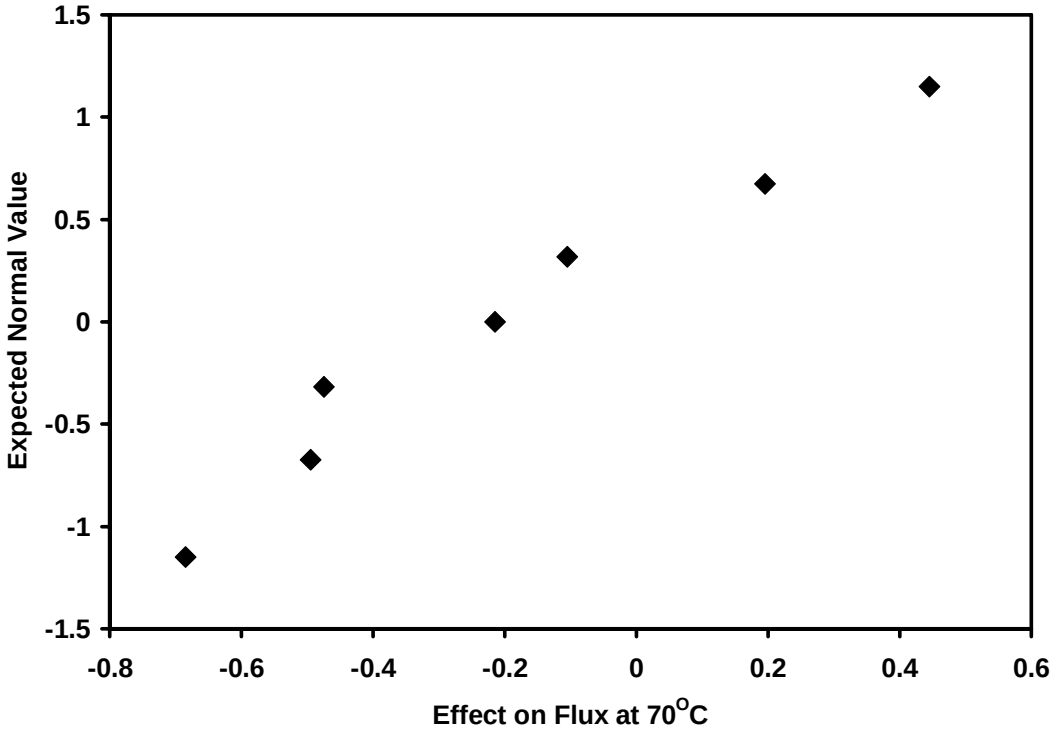



**Figure 5-15. Study of the flux at 70$^{O}$C**

Based on the normal probability plots shown in Figures 5-13 and 5-15, there were no significant effects or significant interactions between these selected factors on the flux of the composite membranes obtained, because all the points on the plots almost formed straight lines. However, all the points in Figures 5-12 and 5-14, instead of forming a straight line, unknowingly formed two different straight lines, just like there are two different populations. It is difficult to explain why there were two straight lines in the plots of Figures 5-12 and 5-14 while there was only one straight line in the plots of Figures 5-13 and 5-15. But according to all experimental data collected, all three factors were not likely to have significant effects on the separation performance of the composite polyelectrolyte membranes with two self-assembled double layers, which means that further tuning the preparation conditions would not significantly improve the separation performance of the composite polyelectrolyte membranes with two self-assembled double layers. Because there were no detectable significant effects and interactions among the variables selected, it was difficult to systematically optimize the preparation

conditions for making the membranes and the separation performance of obtained composite membranes with less than 10 self-assembled double layers. With the preparation conditions suggested in this chapter, it is possible to make good self-assembled composite membranes with less than 10 double layers for the dehydration of IPA/water mixtures.

## 5.3 Summary

In this chapter, the effects of the hydrolysis conditions of porous PAN membranes, the polyelectrolytes used and the fabrication conditions on the separation performance of composite polyelectrolyte membranes have been discussed on the basis of one-factor-at-a-time and through a factorial design. The following is a summary of the main observations:

1. A high charge density polyelectrolyte pair needed to be used to obtain a composite polyelectrolyte membrane with a good selectivity.
2. The molecular sizes of polyelectrolytes should be much larger than the pore size of the porous substrate used. With suitable polyelectrolytes and porous substrates, composite membranes with less than 10 self-assembled double layers could be produced.
3. A composite membrane with improved separation performance might be obtained with dynamic deposition at $80^{O}C$.
4. There were no significant effects and interactions among the hydrolysis temperature, deposition time and post-treatment temperature.

# CHAPTER 6

# EFFECTS OF OPERATING CONDITIONS ON THE PERFORMANCE OF MEMBRANE WITH 2 DOUBLE LAYERS

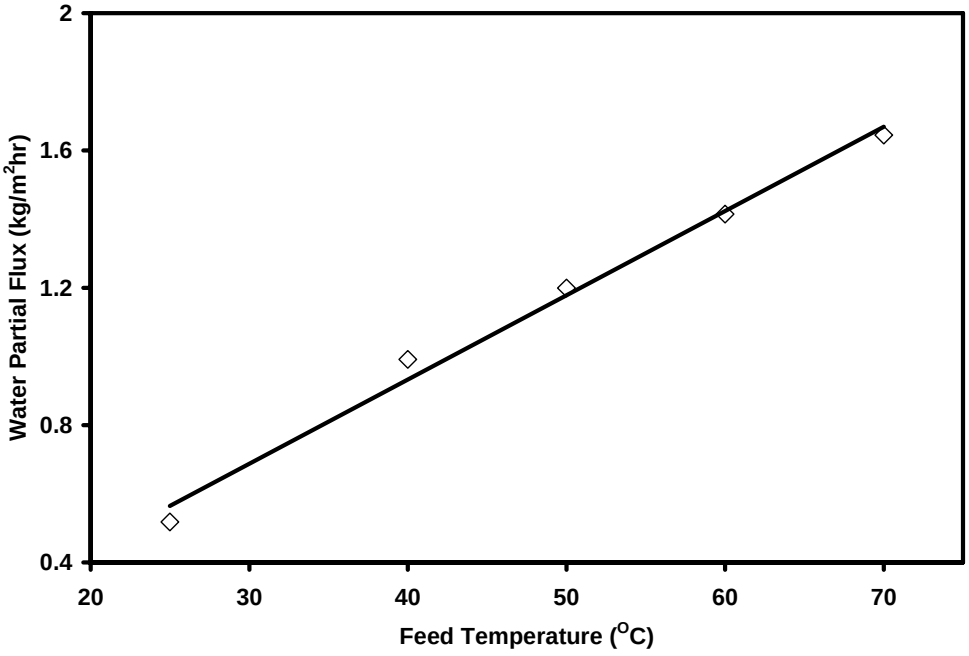
The effects of membrane preparation conditions on the separation performance of the composite polyelectrolyte membranes have been discussed, but the effects of operating conditions on the separation performance of the membranes have not been discussed. The polyelectrolyte composite membranes with 2 double layers developed in previous work seemed to be promising membranes for the dehydration of IPA/water mixtures. In this chapter, the effects of operating conditions on the separation performance of composite polyelectrolyte membranes with 2 double layers will be discussed. The objective of this chapter was to find whether the composite membranes developed in this work could be used for practical applications.

# 6.1 Effect of feed temperature

The feed temperature or the operating temperature is an important operating condition, and the feed temperature has direct impact on the dehydration performance of all membranes. The effect of feed temperature on the dehydration performance of the composite membranes with 2 double layers is shown in Figure 6-1.

Generally speaking, as feed temperature increases, the structure of a pervaporation membrane will become less compact because of swelling. As a result, the permeation rate of the membrane will increase and the selectivity (or the water concentration in permeate) will decrease. However, the composite polyelectrolyte membranes with 2 self-assembled double layers behaved quite differently from conventional pervaporation membranes (see Figure 6-1). As the feed temperature increased, the water partial flux through the membranes with 2 double layers increased, while the IPA partial flux, at the same time, decreased, leading to an increase in membrane selectivity. For example, when the feed temperature increased from $25^{O}C$ to $70^{O}C$, the total flux of the composite membrane increased from 0.57 $kg/m^2hr$ to 1.65 $kg/m^2hr$, while the water concentration in permeate also increased. When the feed temperature was $25^{O}C$, the water concentration in permeate was 90.8 wt%. When the feed temperature was $70^{O}C$, the water concentration in permeate was above 99.0 wt%. The selectivity of the membrane was improved as the feed temperature increased.

As the feed temperature increases, the solubilities and diffusivities of both water and IPA in the separating layer of the polyelectrolyte composite membrane will increase. If the effect of feed temperature on IPA is more significant than on water, then the selectivity of the membrane will decrease as the feed temperature increases. The fact was that the separation performance of the self-assembled composite membranes tested increased as the feed temperature increased. Possible reason for this unusual change is the self-repairing function of the self-assembled separating layer. The self-repairing of defects by the conformation change of polyelectrolytes in a self-assembled separating



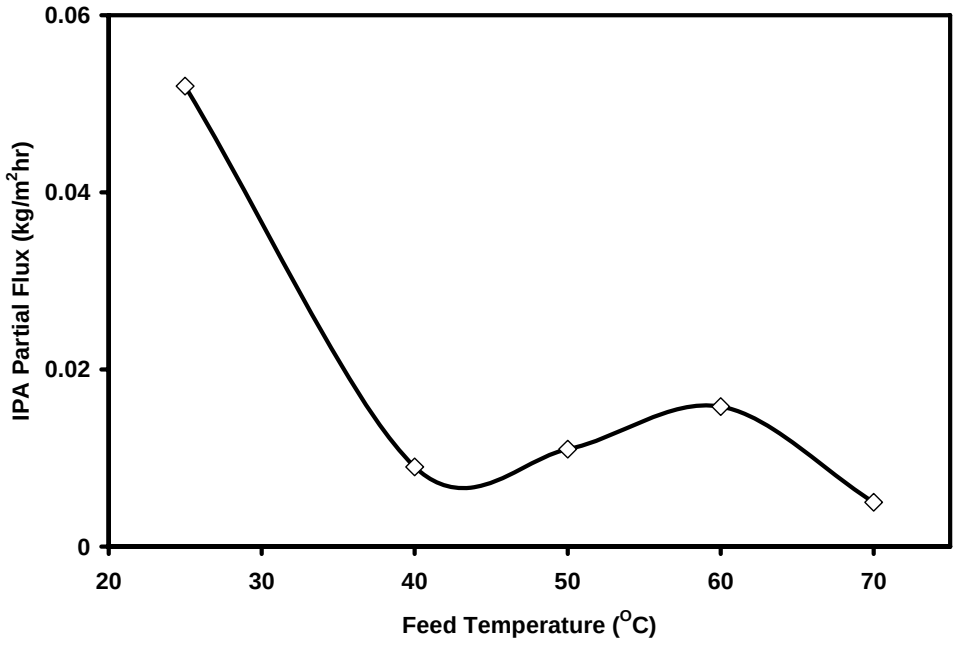




**Figure 6-1. Effect of feed temperature on the partial fluxes of water and IPA for membranes with 2 double layers**

layer can increase the selectivity of the membrane. This is supported by the results shown in Figure 4-10 where when the feed temperature returned to room temperature from $70^{O}C$, the water concentration in permeate was still over 98 wt%. But for the same membrane, the water concentration in permeate was much lower than 98 wt% at room temperature when a heating-cooling cycle started. This indicates that the membrane selectivity had been improved in a pervaporation process, and this improvement was not reversible and this improvement was due to the reduced defects in the membrane.

An Arrhenius-type equation can be used to represent the empirical relationship between the permeation flux (J) and feed temperature [Feng & Huang, 1996]. The apparent activation energy of permeation can be estimated using an lnJ vs. 1/T plot, as shown in Figure 6-2. The apparent activation energy for water permeation through a polyelectrolyte membrane with 2 double layers was calculated to be 21.3 kJ/mol. Huang et al. [2000] reported that the apparent activation energy through different polyelectrolyte membranes was between 30.61 and 9.78 kJ/mol when the feed contained 10% of water and 90% of IPA. It should be mentioned that the total flux was used in Huang's work to calculate the apparent activation energy of permeation. Theoretically, a partial flux should be used to calculate the apparent activation energy of permeation for a given component. But if the membrane is highly selective, the water partial flux will be very close to the total flux. Therefore, the apparent activation energy calculated from the water partial flux is very close to that calculated from the total flux. The apparent activation energy of permeation of the composite membranes with 2 self-assembled double layers was in the range of the apparent activation energy of permeation reported in the literature, which means that the temperature dependence of the permeation flux in a self-assembled membrane was similar to that in other polyelectrolyte membranes.

It was difficult to make an lnJ vs. 1/T plot for the permeation of IPA in the membrane with 2 double layers because the IPA partial flux did not change monotonically as the feed temperature increased. As the feed temperature increases, both the solubility and diffusivity of IPA in the separating layer will increase, and the IPA partial flux, theoretically, will increase. On the other hand, as feed temperature increases, the conformation change in the separating layer of the composite membrane will make

the separating layer denser and less defective and the IPA partial flux will decrease. Experimental error can also cause problems. All these could be used to explain the trend of the IPA partial flux in Figure 6-1. Because there was no linear relationship between the IPA partial flux and feed temperature, it is not possible to calculate the apparent activation energy for IPA permeation.

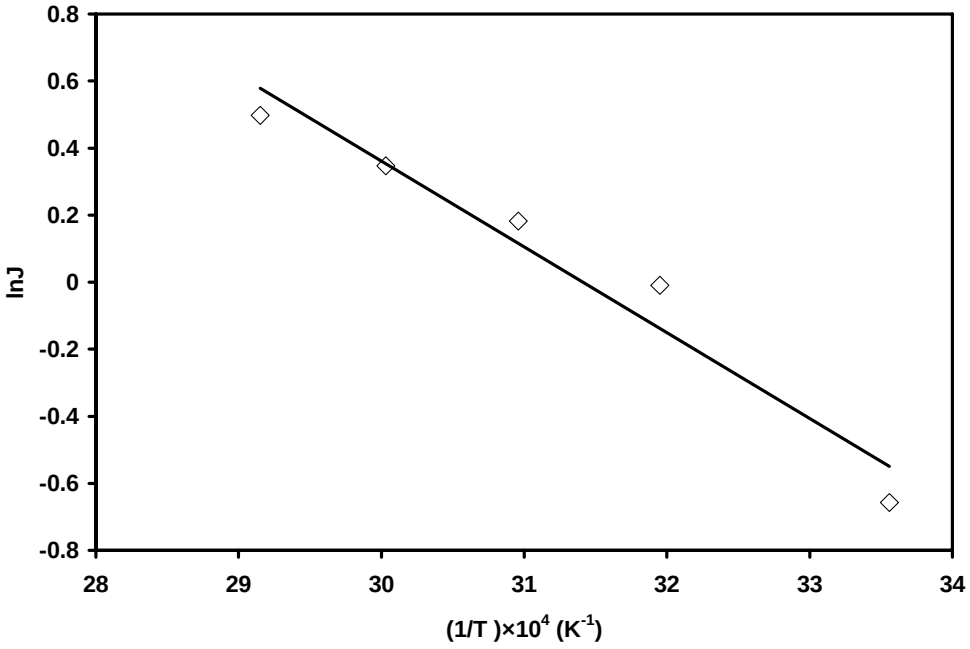



**Figure 6-2. Ln J vs. 1/T for water permeation through a membrane with 2 double layers**

# 6.2 Effect of feed concentration

The effect of feed concentration on the dehydration performance of the composite membrane with 2 self-assembled double layers is shown in Figure 6-3, where the water concentration in the feed varied from 8.0 to about 35.0 wt%. The experiments were carried out at $25^{O}C$ temperature. Note that the separation performance of the membranes was only determined with a feed that contained less than 35.0 wt% of water because pervaporation would not be competitive with distillation if feed water concentration was too high.

As the water concentration in the feed increased, more water would be adsorbed by the highly hydrophilic polyelectrolyte separating layer and then diffused through the membrane, resulting in an increase in the water permeation rate. However, the flux of the composite polyelectrolyte membrane with two self-assembled double layers was not dramatically affected by the feed temperature. At $25^{O}C$ and a feed water content of 30.0 wt%, the flux was 1.0 $kg/m^2hr$, which was high but still not as high as expected. The thickness of a self-assembled separating layer with 2 double layers could be considered to be less than 50 nm, the flux of the membrane should be several times higher than 1.0 $kg/m^2hr$ at a feed water content of 30.0 wt%. One possible reason for the relatively low flux of the composite membrane is that deposited polyelectrolytes have more chances to enter the pores on the porous substrate as water concentration in the feed increases. The higher the water concentration in the feed, the more a polyelectrolyte separating layer swell and the easier the polyelectrolyte molecules in a separating layer enter the pores. When the polyelectrolyte molecules enter the pores by conformation changes, the mass transport resistance through the pores will increase and the permeation flux will decrease. Recall that in Figure 4-8, when the experimental temperature was room temperature, the flux was almost constant as time progressed. But if the feed contains a high percentage of water, the flux of the composite membrane may not be constant anymore at room temperature. To verify this, the water concentration in feed was changed from 30.0 wt% back to about 10.0 wt% and it was found that, at this time, the flux of the given

membrane was about 0.2 kg/m$^2$hr. The original flux was about 0.4 kg/m$^2$hr when the water concentration in the feed was 10 wt%. The compaction of the separation layer due to polyelectrolyte conformation change can reduce the flux of the self-assembled composite membrane.

At room temperature, when the water concentration in the feed was about 12 wt% (this is roughly the composition of an IPA/water azeotrope), the flux of the composite membrane with 2 self-assembled double layers was over 0.4 kg/m$^2$hr and the water concentration in permeate was above 96.0 wt%. If the feed temperature is 80$^O$C, the flux of the membrane with 2 double layers is expected to be close to or over 2 kg/m$^2$hr. It is suggested that if this membrane is used for the dehydration of an IPA/water azeotrope at 80$^O$C, the flux of this membrane will be over 2 kg/m$^2$hr, which is very attractive for IPA dehydration in an industrial scale.

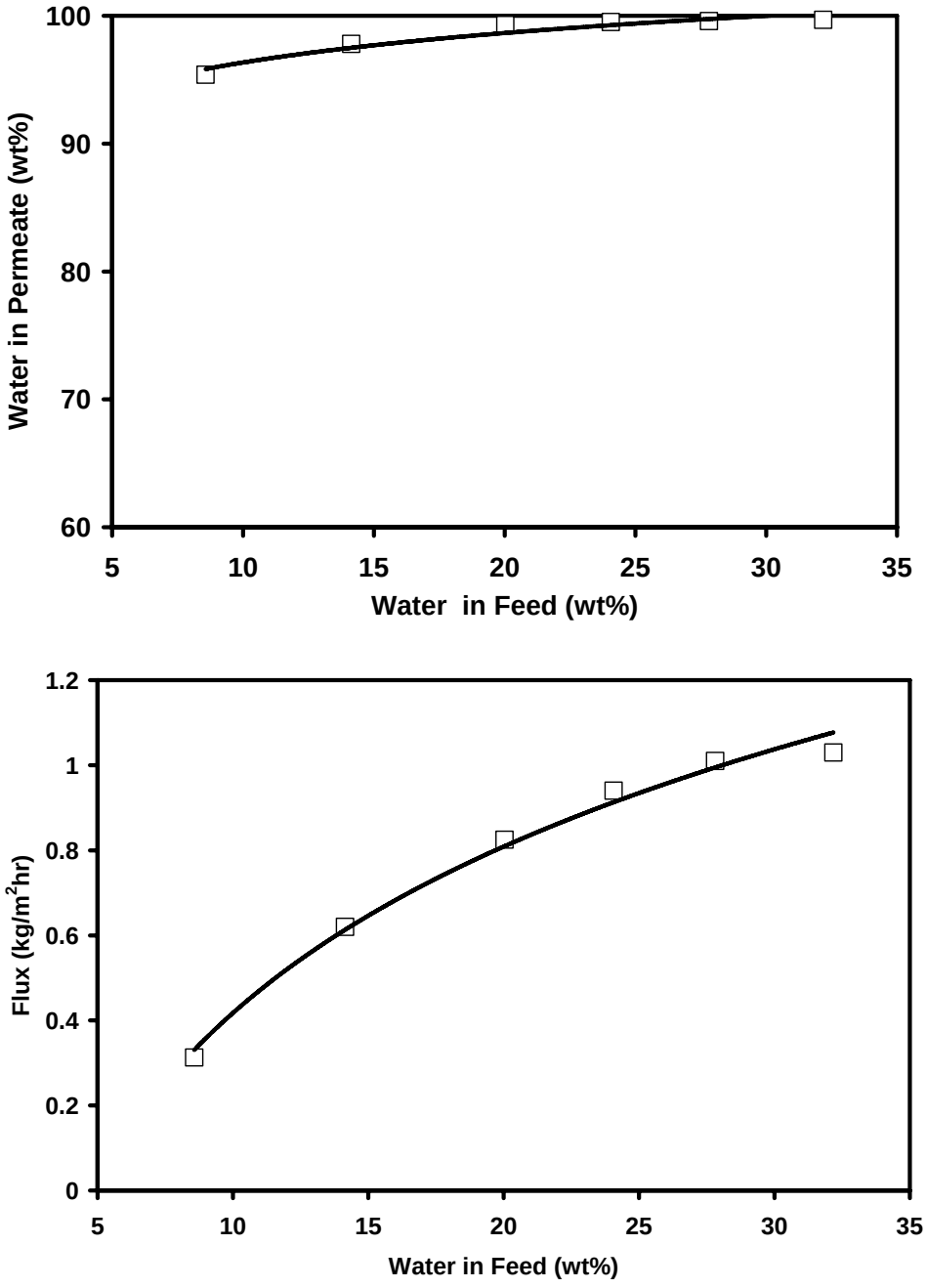



**Figure 6-3. Effect of feed concentrations on the separation performance of the composite membrane with 2 double layers at 25°C**

## 6.3 Stability of membranes with 2 double layers

If the stability of a membrane is not good enough, the flux of the membrane will increase and the selectivity will decrease with time. The separating layer in a composite polyelectrolyte membrane with 2 double layers is very thin (although it is much thicker than expected because of the penetration of the polyelectrolyte chains in the pores of the supporting layer, it is still very thin), and the conformations of the polyelectrolytes in the thin separating layer can easily change during pervaporation. Therefore, the separation performance of a composite polyelectrolyte membrane with 2 double layers can change during pervaporation. It has been shown that the flux of a composite membrane with 2 self-assembled double-layers decreased as a dehydration process proceeded (see Figure 4-8).

Figure 6-4 shows that as time passed the flux of the membrane with 2 double layers decreased while the selectivity of the membrane remained almost the same. For example, the flux at $70^{O}C$ was about 1.98 $kg/m^2hr$ with a feed containing 9.0wt% of water in day 1 and the flux was reduced to 1.69 $kg/m^2hr$ in day 2. The selectivity of the membrane did not change significantly. The reduction in flux has been explained with the conformation change of the deposited polyelectrolytes in the membrane. It is expected that the flux of the membrane will stabilize after a certain period of time. Figure 6-5 shows how the performance of the membrane changed in 4 days. It can be seen that the performance of the membrane with 2 double layers was almost stabilized in about 4 days.

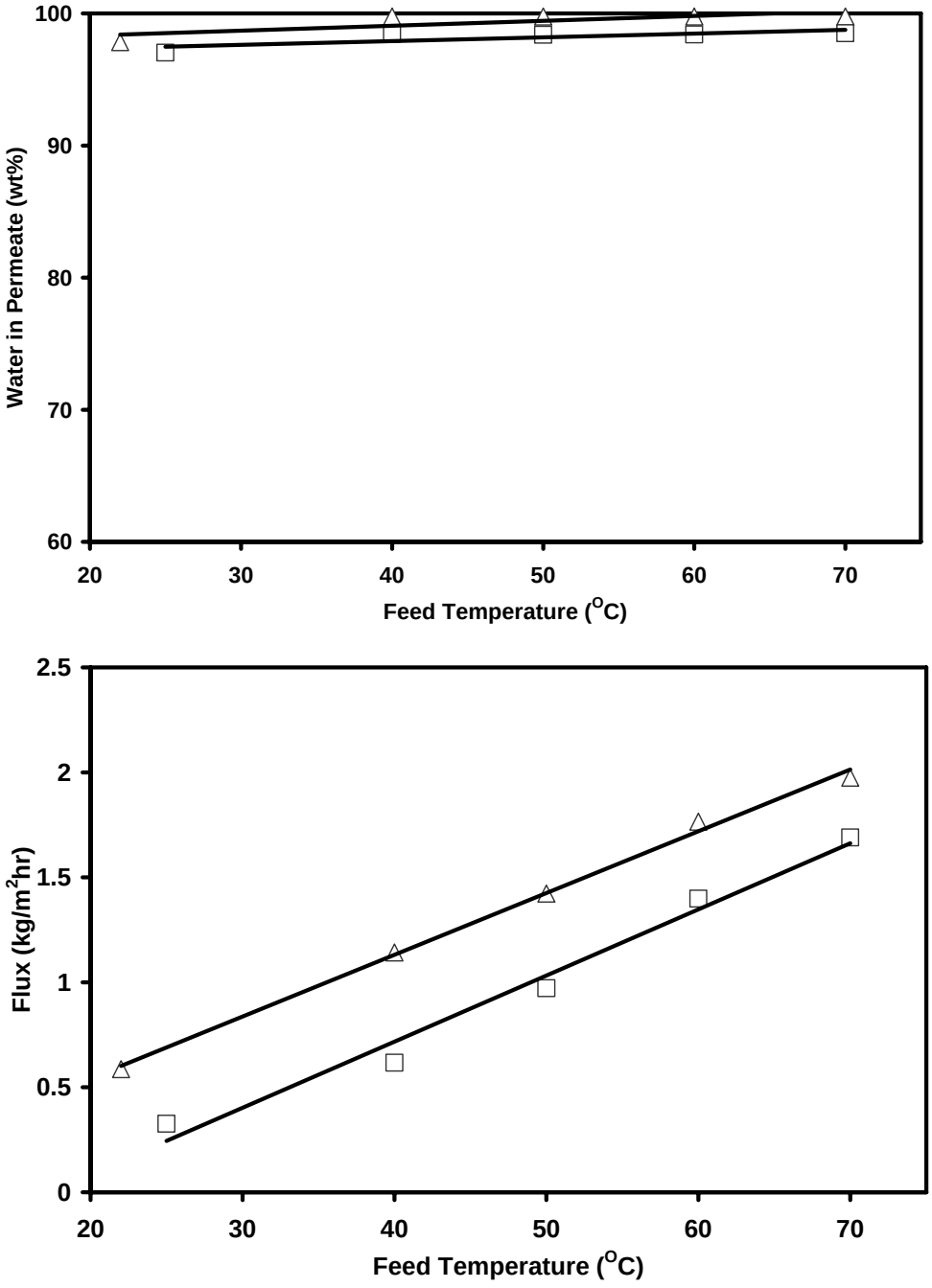



**Figure 6-4. The separation performance of the membrane with 2 double layers**

Δ:Day 1 □: Day 2

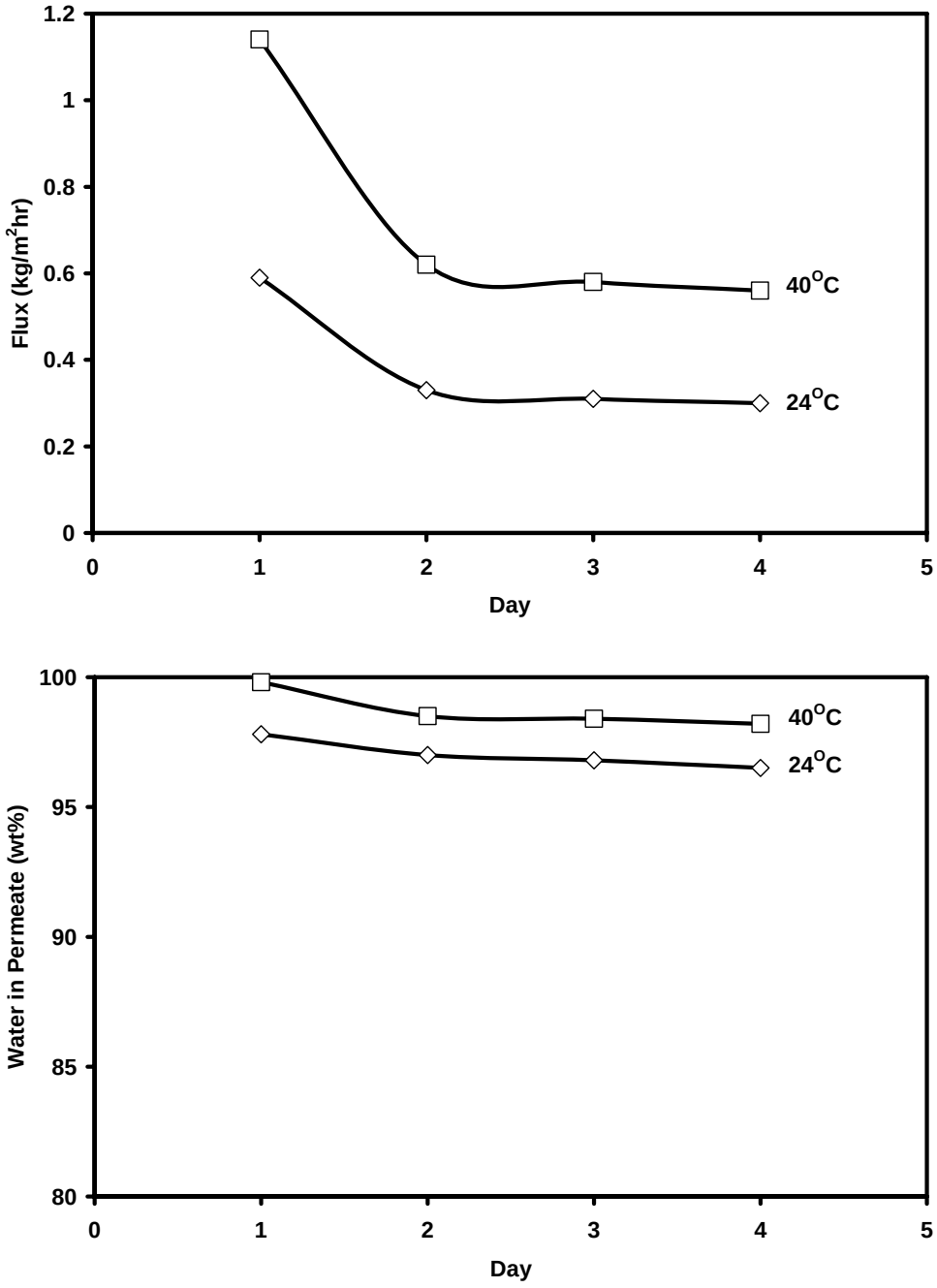



**Figure 6-5. The stability of the separation performance of the membrane with 2 double layers**

It should be stressed that the composite membrane with 2 self-assembled double layers was structurally stable although the membrane permeation rate declined initially. If the membrane was not stable, the membrane would continue to degrade with time. The flux of the membrane would continuously increase and the selectivity would continuously decrease. This is apparently not the case for the composite membrane with 2 self-assembled double layers. Actually, the permeation flux of the membrane decreased while the selectivity remained almost the same. This demonstrates that the polyelectrolyte membrane with 2 double layers was stable.

## 6.4 Separation performance comparison between the composite membranes with 2 self-assembled double layers and other reported membranes

Figure 6-6 is a comparison of separation performance of four different composite pervaporation membranes: (1). A composite polyelectrolyte membrane with 2 self-assembled double layers developed in this work, (2). A commercial PVA composite membrane made by Sulzer [Will & Lichtenthaler, 1992], (3). A composite polyelectrolyte membrane (polyethylenimine + poly(acrylic acid )) with 7 double layers [Meier-Haack et al., 2001], and (4). A composite polyelectrolyte membrane (polyvinylamine + polyvinylsulfate) with 60 double layers [Toutianoush & Tieke, 2002]. It is obvious that the separation performance of the composite polyelectrolyte membrane with 2 self-assembled double layers developed in this work is much better than the separation performance of the commercial PVA composite membrane. For example, at $25^{O}C$ and a feed water content of 15 wt%, the flux of the composite membrane with 2 self-assembled double layers was over 0.6 $kg/m^2hr$ and the water concentration in permeate was 97.8 wt%, while at $60^{O}C$ for the same feed composition, corresponding performance data for a commercial PVA membrane were only 0.35 $kg/m^2hr$ and 97.0 wt%, respectively.

It should be mentioned that the reported separation performance shown in Figure 6-6 was at different temperatures for different membranes. Tieke's membranes were only tested at 58.5$^{O}$C, while Meier-Haack's membranes were only tested at 50$^{O}$C.

The composite membrane with 2 self-assembled double layers appeared to have better permselectivity than the other two polyelectrolyte self-assembled composite membranes reported in the literature. When the water concentration in feed was 10.0wt%, the flux of the composite self-assembled membrane made by Meier-Haack et al. was less than 0.1 kg/m$^2$hr (at 50$^{O}$C), and the flux of Tieke's membrane was about 0.7 kg/m$^2$hr (at 58.5$^{O}$C). The flux of the composite membrane with 2 double layers was 0.4 kg/m$^2$hr (at 25$^{O}$C). It is evident that the composite membrane developed in this work was much more permeable than Meier-Haack's membrane. It would be nice to compare the fluxes of different membranes at the same operating conditions. Unfortunately the operating conditions used by different researches were different. In Figure 6-7, the dehydration performance of the membrane with 2 double layers (at 60$^{O}$C) is compared with the dehydration performance of Tieke's membrane (at 58.5$^{O}$C).

It is easy to understand that Tieke's composite membrane had a higher flux than the commercial PVA membrane because Tieke's membrane had a relatively thin separating layer. Meier-Haack et al. used a non-porous substrate to make a composite membrane, and the permeation resistance in a non-porous substrate was much higher than in a porous substrate. The flux of a composite membrane with a non-porous substrate is usually much lower than that of the membrane with a porous substrate. Both the composite membranes developed in this work and the membranes developed by Tieke's group were self-assembled composite membranes with porous substrates, but with different numbers of double layers in the separating layers. The composite membrane developed in this work and tested for performance comparison had 2 double layers only, while Tieke's membrane had 60 double layers. If the thickness of a single polyelectrolyte layer in these two membranes is the same, the permeation resistance of Tieke's membrane will be 30 times higher than that in our membrane. The flux of the composite membrane with 2 double layer developed in this work was therefore higher than that of Tieke's membrane.

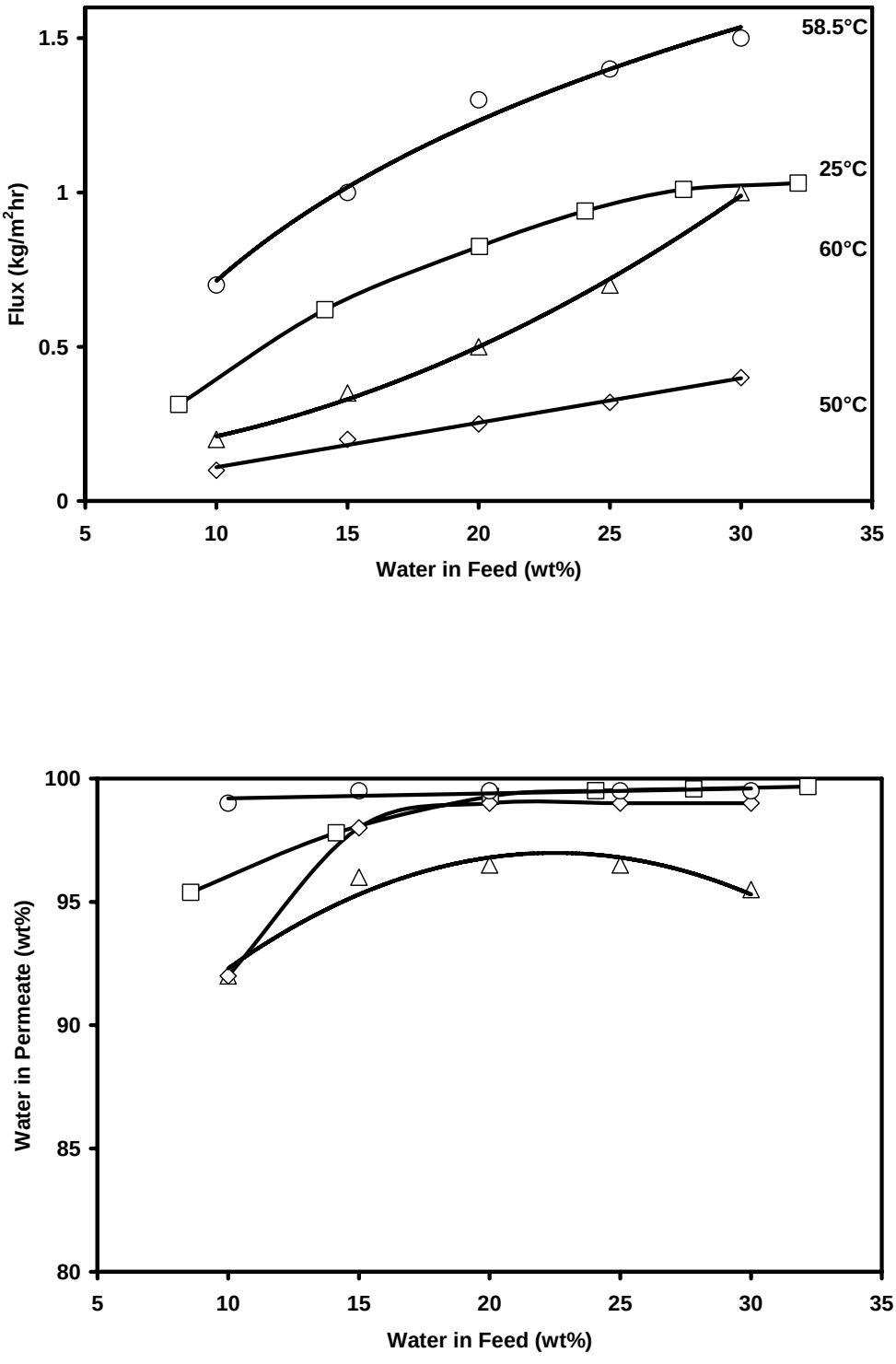



**Figure 6-6. A comparison of membrane performance for IPA dehydration**

□: Composite polyelectrolyte membrane with 2 self-assembled double layers developed in this work, (polyethylenimine + poly(acrylic acid ), 25$^{O}$C

Δ: Sulzer commercial composite PVA membrane [Will & Lichtenthaler, 1992], 60$^{O}$C

◊: Meier-Haack's composite polyelectrolyte membrane with 7 double layers (polyethylenimine + poly(acrylic acid )) [Meier-Haack et al., 2001], 50$^{O}$C

○: Tieke's composite polyelectrolyte membrane with 60 double layers (polyvinylamine + polyvinylsulfate) [Toutianoush & Tieke, 2002], 58.5$^{O}$C

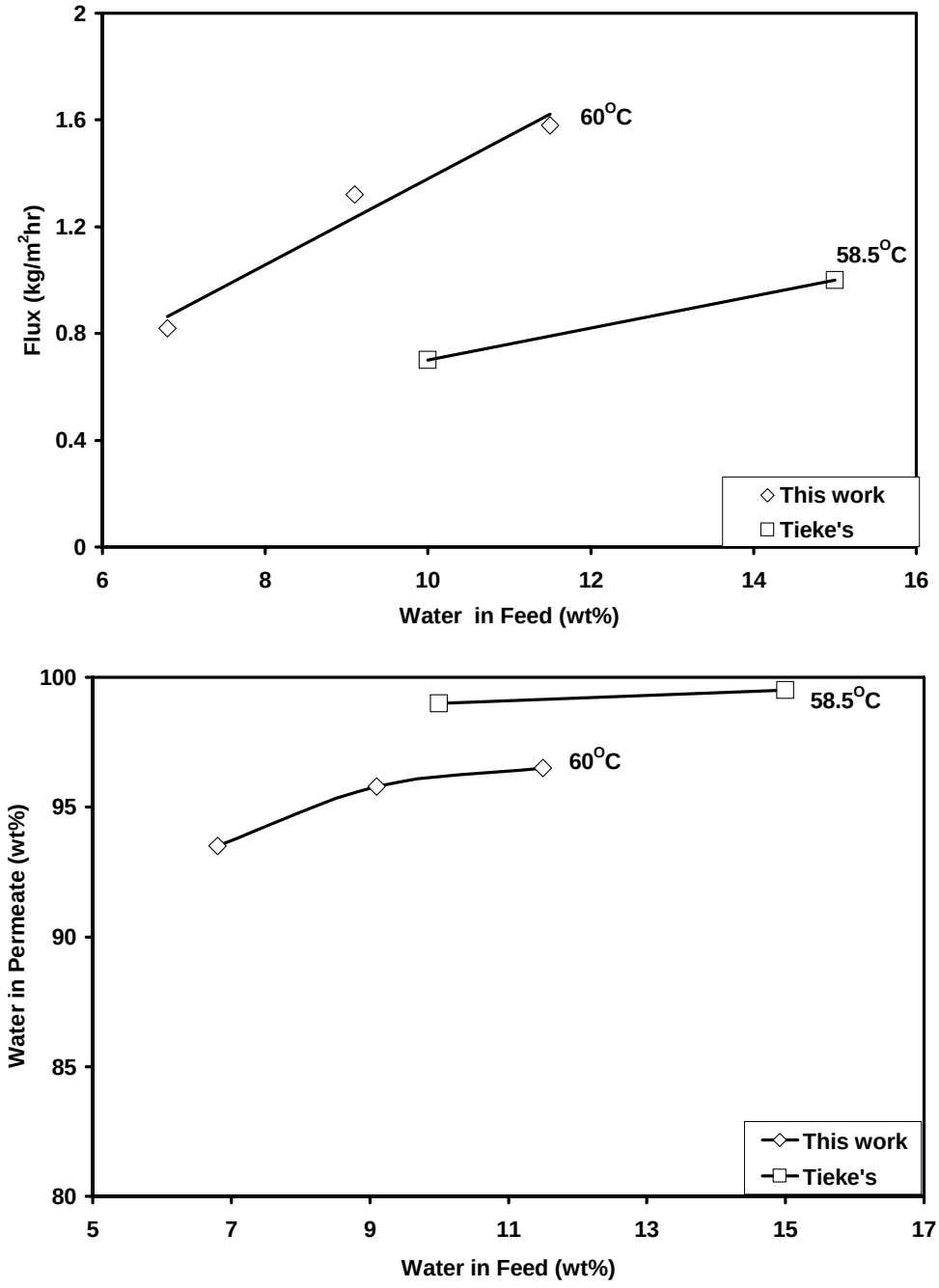



**Figure 6-7. Comparison between the dehydration performance of the membrane with 2 double layers and that of Tieke's membrane**

It should be emphasized that the thickness of a single polyelectrolyte layer deposited in this work could be different from that in Tieke's membranes. In this work, polyelectrolytes with high molecular weights and porous substrates with the pore sizes less than 10 nm were used for depositions and the polyelectrolyte molecules had fewer chances to enter the pores on the porous substrate. In contrast, polyelectrolytes with relatively low molecular weights and a porous substrate with a large pore size (20-200 nm) were used by Tieke et al.. Therefore, the polyelectrolyte molecules could easily penetrate into the pores in Tieke's work. As a result, the thickness of a single deposited layer in Tieke's membrane was expected to be thicker than that in this work because of different degrees of penetration. The multilayer with 60 double layers developed by Tieke et al. should be much thicker than the multilayer with 2 double layers developed in this work because of different degrees of penetration and different numbers of double layers. Therefore, it is reasonable that Tieke's membranes had a lower flux than the membrane with 2 double layers developed in this work.

The selectivity of Tieke's membranes was better than that of the membrane developed in this work as shown in Figure 6-7, though the selectivity of the composite membranes developed in this work, from an application point of view, was fairly good. There are two reasons for the selectivity difference between these two membranes. First, Tieke's membrane had 60 double layers and all the pores on the porous substrate were believed to be completely covered by polyelectrolyte complex through pore filling and then pore bridging. In this work, all pores were covered by polyelectrolyte complex but small defects could exist because of limited number of depositions. Defects would lead to a higher flux and a lower selectivity. Secondly, polyvinylamine, which was used as a polycation for deposition in the literature, had a higher charge density than polyethylenimine. Thus, Tieke's composite membrane was expected to have a higher selectivity than the composite membranes developed in this work. The polyelectrolyte pair used by Meier-Haack et al. was the same as that used in the present work, and the selectivity of Meier-Haack's membrane was therefore also lower than that of Tieke's membrane. Tieke's membrane had the highest selectivity among these three polyelectrolyte composite membranes.

Although the selectivity of the composite membrane with 2 self-assembled double layers was lower than that of Tieke's membranes, the composite membrane developed in this work had still a relatively high selectivity and a high flux. More importantly, the fabrication of Tieke's composite membranes was too time-consuming for practical manufacturing while the fabrication of the membrane with 2 double layers is simple and the membrane holds promise for the dehydration of IPA/water mixtures.

## 6.5 Summary

The effects of operating conditions on the separation performance of the self-assembled composite membrane with 2 double layers have been studied and the separation performance of the membrane has been compared with that of other membranes reported in the literature in this part. The followings are the main points of this part:

1. The permeation flux of water through the self-assembled membrane with 2 double layers had similar dependence on the feed temperature to that of other polyelectrolyte-based membranes reported.
2. The selectivity of the self-assembled membrane with 2 double layers unusually increased when feed temperature increased. The conformation change of the deposited polyelectrolytes could be used to explain this behavior.
3. The composite membrane had good stability in the period of experiment.
4. The overall separation performance of the membrane with 2 double layers was better than that of other reported membranes, and the membrane is a good candidate for practical dehydration of IPA/water mixtures.

# CHAPTER 7

# CONCLUSIONS /CONTRIBUTIONS TO ORIGINAL RESEARCH AND RECOMMENDATIONS FOR FUTURE WORK

## 7.1 Conclusions

Based on the experimental results collected, the following conclusions can be drawn:

- The hydrolyzed porous PAN membranes could be used as porous substrates to make composite membranes with self-assembled polyelectrolyte separating layers.
- The number of self-assembled double layers in a composite membrane with good separation performance could be reduced effectively by using high molecular weight polyelectrolytes, a porous substrate with relatively small pores and by using the concentration-changing deposition technique.

- Polyelectrolyte coils in the deposition solutions can enter or even pass through the pores on a porous substrate if the molecular sizes of the polyelectrolytes are sufficiently small. Most polyelectrolytes can be adsorbed onto the inner surface to reduce the size of the pores if the molecular sizes are not too small. When the polyelectrolyte molecules enter the pores, the thickness of a self-assembled multilayer can hardly be controlled.
- The composite membranes with less than 10 self-assembled double layers could be fabricated with suitably selected materials and preparation conditions. The lowest number of self-assembled double layers in a composite membrane was 2, and this composite membrane still had good separation performance for the dehydration of IPA/water mixtures.
- Most pre-selected parameters involved in membrane preparation (listed in Table 3-17) are reasonable for the fabrication of composite membranes with less than 10 self-assembled double layers.
- High molecular weight polyelectrolytes and porous substrates with relatively small pores were needed for making composite membranes with less than 10 self-assembled double layers. In addition, polyelectrolytes with high charge densities were required for making polyelectrolyte membranes with high selectivities.
- The reproducibility of composite membranes with less than 10 double layers was not very good. However, the average performance data of several membranes made under the same conditions and with the same batch of hydrolyzed substrate were fairly repeatable. The relatively poor reproducibility of the composite membranes resulted from the poor controllability of the thickness of the first several depositions on a porous substrate, and random defects also affected the membrane reproducibility.
- Depending on the molecular sizes of polyelectrolytes and the pore size of a porous substrate, the penetration of polyelectrolyte molecules in the pores can be negligible, limited and significant. A two-stage process is suggested for the formation of a self-assembled multilayer on either a

porous or a non-porous substrate. Generally speaking, polyelectrolyte molecules will first fill the pores to make the porous substrate "non-porous", then polyelectrolyte molecules will deposit on a "non-porous" substrate to build a self-assembled multilayer.

- The composite membranes developed in this work had high fluxes and relatively high selectivities for the dehydration of IPA/water mixtures. Because reduced number of depositions is needed to make a defect free membrane, significant time savings are achieved in the membrane fabrication. Therefore, the self-assembled composite membranes with less than 10 double layers developed in this work are promising for industrial applications.

# 7.2 Contributions to Original Research

## 7.2.1 Hydrolyzed porous PAN membrane — a new charged porous material for making self-assembled membranes (Chapter 3)

There are many reports in the literature regarding the use of electrostatic self-assembly technique to make self-assembled multilayers, but in most studies polished and non-porous silicon wafers were used as the substrates for depositions.

For pervaporation membrane applications, a self-assembled multilayer has to be built on a porous substrate in order to get relatively high permeation flux. Hydrolysis was used in this work to treat the surface of porous PAN membranes for self-assembly depositions. The hydrolysis of a porous PAN membrane converts -CN groups into carboxyl groups. Only the –CN groups on the membrane surface will be converted into carboxyl groups if the hydrolysis conditions are controlled properly. Surface hydrolysis will not affect the mechanical strength of the supporting membrane and will not affect the

adhesion between the hydrolyzed PAN layer and the polyester backing material, which will endow the composite membrane with good stability. Hydrolyzed PAN membranes are permanently charged membranes, which will also give composite polyelectrolyte membranes a long lifetime.

This is the first time that a hydrolyzed porous PAN membrane is used as a porous substrate to make self-assembled separating layers for composite membranes. Experimental data showed that the hydrolyzed porous PAN membranes could be used as porous substrates to make composite membranes and the composite membranes using the hydrolyzed porous PAN membranes as porous substrates had good separation performance for the dehydration of aqueous IPA solutions.

### 7.2.2 Concentration-changing deposition technique — a new technique to reduce the number of double layers in a composite membrane (Chapter 3)

In all literature work reported to date, constant concentrations of polyelectrolyte solutions were always used throughout the deposition processes. The concentration-changing deposition technique developed in this work is a new idea to reduce the number of depositions needed in a composite membrane. Experimental data demonstrated that it was effective to use the concentration-change deposition technique to reduce the number of depositions needed for making a composite membrane.

### 7.2.3 Method of fabricating a self-assembled membrane — a new way to make self-assembled composite membranes more practical (Chapters 4 and 5)

Self-assembled composite membranes for pervaporation applications have been reported in the literature. Both non-porous and porous substrates have been used for the fabrication of self-assembled composite membranes in the literature. Because the fluxes

of the composite membranes made with non-porous substrates are generally too low to be practical, porous substrates have to be used for the fabrication of self-assembled composite membranes for practical applications.

Self-assembled composite membranes are promising for dehydration applications, the reported method for making such composite membranes, unfortunately, is not practical because it needs as many as 60 double-layers to make a separating layer for a membrane. It takes more than 60 hr to make a separating layer and this fabrication process is too time-consuming. To make self-assembled composite membranes practical, the number of double layers in the separating layer of a composite membrane has to be reduced significantly.

In this work, we tried to reduce the number of depositions needed in a membrane by using polyelectrolytes with high molecular weights and a porous substrate with a small pore size. Using a suitable substrate and suitable polyelectrolytes under appropriate preparation conditions, self-assembled membranes with less than 10 double layers have been developed. The fabrication method used in this work to make composite membranes is simple and it makes the self-assembled pervaporation membrane more practical.

### 7.2.4 Membrane with as few as 2 double layers — a new high performance membrane for IPA dehydration (Chapter 6)

The flux of the composite membrane made by Tieke's group is not high because of the penetration of polyelectrolyte molecules in the porous substrate. By applying carefully selected conditions, the number of depositions required by a composite membrane has been reduced substantially. The composite membrane with 2 double layers developed in this work had very good separating performance. The flux of the composite membrane (at $60^{O}$C and 9.0 wt% water in feed for IPA dehydration) was 2 times higher than that of the composite membrane developed by Tieke et al. while the membrane selectivity of the composite membrane was fairly good. The composite membrane with 2

self-assembled double layers is a promising membrane for the dehydration of water/IPA mixture practically.

### 7.2.5 Two-stage process — a qualitative description for the formation of a self-assembled multilayer on a porous substrate (Chapter 3)

The formation of a self-assembled multilayer on a porous substrate has not been well described. Based on the separation performance of different membranes made from different porous substrates and different polyelectrolyte molecules, a two-stage process for the formation of a self-assembled multilayer on a porous substrate has been suggested. This is a general description for the formation of a self-assembled multilayer on either a porous or a non-porous substrate. This description takes into account the penetration of polyelectrolyte molecules in a porous substrate and such a penetration has been essentially neglected in the literature.

## 7.3 Recommendations

The followings are recommended for future studies.

The stability of the composite membranes with less than 10 self-assembled double layers affects their practical application. The stability of the composite polyelectrolyte pervaporation membranes, from a flux point of view, was not very good because the flux of a self-assembled composite membrane decreased with time. The flux stability of self-assembled composite membranes needs to be improved further for commercial applications. The reason for the relatively low flux stability is the conformation change of the polyelectrolytes in the separating layer. In order to improve the flux stability of the composite membranes, the structure of each self-assembled polyelectrolyte double layer needs to be stabilized further. A covalently attached self-assembly multilayer has been reported in the literature [Chen & Cao, 1999]. If suitable polyelectrolytes can be found for making self-assembled polyelectrolyte double layers that can further form covalent bonding between layers to stabilize the conformations of the polyelectrolytes, then the flux stability of the composite polyelectrolyte pervaporation membrane will be further improved.

The focus of this work was the separation performance of composite polyelectrolyte membranes and how to practically make the composite membranes with good separating performance. The actual structure of the self-assembled polyelectrolyte double layers has not been characterized. More structural characterization work, such as $\zeta$ potential, atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) etc., can be done to better understand the membrane structure.

The self-assembly of polyelectrolytes on a porous substrate preferably occurs on one side of the substrate because the membrane made with two-sided deposition has poor mechanical strength and poor separation performance. When a flat sheet hydrolyzed porous PAN membrane was used as a porous substrate for self-assembly depositions, a

special technique (bottle deposition technique in this work) had to be used to prevent the depositions on the backside. But bottle deposition technique cannot bee used for industrial production and it is necessary to find a new way to make one-sided deposition for large scale production. If a porous hollow fiber membrane is used as a porous substrate for the self-assembly depositions of polyelectrolyte, it will be easy to perform one-sided depositions on the outer surface of the hollow fibers. An additional advantage of using hollow fiber substrates is that hollow fibers can be easily packed into a module. For industrial applications, this is important because it will reduce the cost of module fabrication. It is worth trying to use porous hollow fibers as substrates to make polyelectrolyte composite membranes using the electrostatic self-assembly technique.

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# APPENDICES

## A1. Pervaporation experimental results of factorial design (see Table 5-2 for factorial design)

| Membrane Number | Pervaporation temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt %) |
|---|---|---|---|
| 1# | 28 | 0.73 | 91.4 |
| | 40 | 1.19 | 94.0 |
| | 50 | 1.67 | 96.8 |
| | 60 | 2.02 | 96.8 |
| | 70 | 2.38 | 96.1 |
| 2# | 27 | 0.20 | 97.3 |
| | 40 | 0.57 | 98.2 |
| | 50 | 0.88 | 98.5 |
| | 60 | 1.26 | 98.6 |
| | 70 | 1.55 | 98.6 |
| 3# | 27 | 0.63 | 99.2 |
| | 40 | 1.04 | 99.3 |
| | 50 | 1.35 | 99.3 |
| | 60 | 1.63 | 99.4 |
| | 70 | 1.85 | 99.2 |
| 4# | 25 | 0.19 | 99.2 |
| | 40 | 0.59 | 99.7 |
| | 50 | 0.87 | 99.8 |
| | 60 | 1.25 | 99.9 |
| | 70 | 1.52 | 99.9 |
| 5# | 28 | 0.71 | 33.3 |

| | | | |
|---|---|---|---|
| | 40 | 1.05 | 36.5 |
| | 50 | 1.44 | 37.6 |
| | 60 | 1.92 | 41.4 |
| | 70 | 2.42 | 41.3 |
| 6# | 28 | 0.40 | 97.9 |
| | 40 | 0.62 | 98.4 |
| | 50 | 0.80 | 98.3 |
| | 60 | 0.92 | 98.3 |
| | 70 | 0.99 | 98.1 |
| 7# | 26 | 0.29 | 98.2 |
| | 40 | 0.57 | 98.9 |
| | 50 | 0.85 | 99.2 |
| | 60 | 0.96 | 99.1 |
| | 70 | 1.07 | 99.1 |
| 8# | 30 | 0.28 | 98.4 |
| | 40 | 0.44 | 99.0 |
| | 50 | 0.59 | 99.6 |
| | 60 | 0.78 | 99.8 |
| | 70 | 0.92 | 99.5 |

## A2. The separation performance of the composite polyelectrolyte pervaporation membranes with 7 self-assembled double layers

| Membrane Number | | Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in Permeate (wt %) | Separation Factor |
|---|---|---|---|---|---|
| | 1 | 22 | 0.23 | 98.8 | 853 |
| | | 40 | 0.39 | 99.8 | 4463 |
| | | 50 | 0.56 | 99.8 | 4463 |
| | | 60 | 0.64 | 99.8 | 4463 |
| | | 70 | 0.72 | 99.8 | 4463 |
| | 2 | 23 | 0.22 | 89.5 | 86 |
| | | 40 | 0.29 | 92.4 | 122 |
| | | 50 | 0.34 | 98.8 | 800 |
| | | 60 | 0.43 | 99.8 | 4463 |
| | | 70 | 0.57 | 99.8 | 4463 |
| | 3 | 23 | 0.19 | 85.8 | 61 |
| | | 40 | 0.24 | 94.7 | 180 |
| Hydrolysis conditions: | | 50 | 0.37 | 97.2 | 349 |
| 75 $^{O}$C | | 60 | 0.39 | 99.0 | 1050 |
| 20 min | | 70 | 0.47 | 99.8 | 4463 |
| 7 double layer | 4 | 24 | 0.24 | 89.5 | 86 |
| 12 hr post treatment | | 40 | 0.35 | 94.1 | 161 |
| Substrate batch 1# | | 50 | 0.48 | 97.4 | 379 |
| | | 60 | 0.64 | 98.6 | 711 |
| | | 70 | 0.72 | 99.3 | 1437 |
| | 5 | 25 | 0.16 | 93.2 | 138 |
| | | 40 | 0.31 | 96.0 | 243 |
| | | 50 | 0.37 | 98.8 | 825 |
| | | 60 | 0.45 | 99.5 | 1984 |
| | | 70 | 0.60 | 99.5 | 1984 |
| | 6 | 25 | 0.14 | 95.1 | 196 |
| | | 40 | 0.34 | 97.3 | 363 |
| | | 50 | 0.47 | 98.4 | 619 |
| | | 60 | 0.53 | 99.5 | 2035 |
| | | 70 | 0.72 | 99.4 | 1685 |
| | | 70 | 0.71 | 99.4 | 1722 |
| | | 70 | 0.69 | 99.3 | 1437 |
| | | 25 | 0.05 | 92.9 | 132 |
| Hydrolysis conditions: | | 40 | 0.10 | 95.8 | 229 |
| 75$^{O}$C and 20 min | | 50 | 0.15 | 96.2 | 255 |
| batch 2 ,average of 2 | | 60 | 0.28 | 98.4 | 640 |
| 7 double layers | | 70 | 0.37 | 99.8 | 4463 |

* The water concentrations in permeates have been rounded up in the appendices. The separation factors in the appendices are calculated with the water concentrations in permeates before rounding up. So it is possible that the water concentrations in permeates are the same while the separation factors are different.

## A3. The separation performance of the composite polyelectrolyte pervaporation membranes with 2 self-assembled double layers

| Membrane sample | Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| | 25 | 0.73 | 81.4 | 44 |
| Hydrolysis conditions: | 40 | 1.57 | 83.4 | 50 |
| 75$^{O}$C and 20 min | 50 | 1.95 | 84.6 | 55 |
| 2 double layers | 60 | 2.38 | 86.6 | 65 |
| | 70 | 2.76 | 85.1 | 57 |
| | 25 | 0.60 | 88.9 | 81 |
| Hydrolysis conditions: | 40 | 1.19 | 91.5 | 109 |
| 75$^{O}$C and 20 min | 50 | 1.51 | 93.7 | 149 |
| 2 double layers | 60 | 1.70 | 94.5 | 173 |
| | 70 | 1.92 | 95.4 | 210 |
| | 22 | 0.61 | 98.5 | 656 |
| Hydrolysis conditions: | 40 | 1.22 | 99.8 | 4463 |
| 75$^{O}$C and 20 min | 50 | 1.57 | 99.8 | 4463 |
| 2 double layers | 60 | 1.87 | 99.8 | 4463 |
| | 70 | 1.99 | 99.8 | 4463 |
| | 25 | 0.57 | 90.8 | 100 |
| Hydrolysis conditions: | 40 | 0.97 | 99.1 | 1094 |
| 75$^{O}$C and 20 min | 50 | 1.21 | 99.1 | 1142 |
| 2 double layers | 60 | 1.43 | 98.9 | 925 |
| Substrate batch 2 | 70 | 1.65 | 99.8 | 4463 |
| Average of 2 | | | | |

## A4. The separation performance of the composite polyelectrolyte pervaporation membranes with different number of self-assembled double layers

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in Permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 20 min 7 double layers | 25 | 0.05 | 93.0 | 134 |
| | 40 | 0.10 | 95.8 | 229 |
| | 50 | 0.15 | 96.2 | 255 |
| | 60 | 0.28 | 98.4 | 640 |
| | 70 | 0.37 | 99.8 | 4463 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 6 double layers | 23 | 0.12 | 65.0 | 18 |
| | 40 | 0.13 | 92.1 | 118 |
| | 50 | 0.23 | 96.1 | 246 |
| | 60 | 0.37 | 98.7 | 768 |
| | 70 | 0.50 | 99.8 | 4463 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 5 double layers | 24 | 0.07 | 97.8 | 445 |
| | 40 | 0.17 | 99.1 | 1125 |
| | 50 | 0.37 | 99.8 | 4463 |
| | 60 | 0.59 | 99.8 | 4463 |
| | 70 | 0.73 | 99.8 | 4463 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 4 double layers | 25 | 0.07 | 88.8 | 80 |
| | 40 | 0.13 | 96.7 | 298 |
| | 50 | 0.31 | 98.4 | 640 |
| | 60 | 0.48 | 98.9 | 892 |
| | 70 | 0.64 | 99.1 | 1078 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 3 double layers | 25 | 0.12 | 78.1 | 36 |
| | 40 | 0.38 | 92.7 | 128 |
| | 50 | 0.61 | 98.2 | 560 |
| | 60 | 0.77 | 98.5 | 668 |
| | 70 | 0.87 | 98.5 | 674 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers | 25 | 0.57 | 90.8 | 99 |
| | 40 | 0.97 | 99.1 | 1094 |
| | 50 | 1.21 | 99.1 | 1142 |
| | 60 | 1.43 | 98.9 | 924 |
| | 70 | 1.65 | 99.8 | 4463 |

## A5. The stability of the separation performance of a composite polyelectrolyte pervaporation membrane

| Membrane sample | Time (hr) | Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt %) | Separation Factor |
|---|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers | 2 | 25 | 0.60 | 95.9 | 239 |
| | 4 | 25 | 0.60 | 96.8 | 306 |
| | 6 | 25 | 0.60 | 96.8 | 309 |
| | 8 | 25 | 0.59 | 97.2 | 351 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers | 2 | 70 | 1.91 | 97.8 | 448 |
| | 4 | 70 | 1.80 | 97.41 | 386 |
| | 6 | 70 | 1.73 | 97.44 | 384 |
| | 8 | 70 | 1.69 | 97.4 | 382 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Day 1 | | 22 | 0.59 | 97.8 | 456 |
| | | 40 | 1.14 | 99.8 | 4463 |
| | | 50 | 1.42 | 99.8 | 4463 |
| | | 60 | 1.77 | 99.8 | 4463 |
| | | 70 | 1.98 | 99.8 | 4463 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Day 2 | | 25 | 0.33 | 97.0 | 331 |
| | | 40 | 0.62 | 98.5 | 651 |
| | | 50 | 0.97 | 98.4 | 619 |
| | | 60 | 1.40 | 98.4 | 629 |
| | | 70 | 1.69 | 98.5 | 668 |
| Day 3 | | 24 | 0.31 | 96.8 | 309 |
| | | 40 | 0.58 | 98.4 | 629 |
| Day 4 | | 23 | 0.30 | 96.5 | 279 |
| | | 40 | 0.56 | 98.2 | 560 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 3 double layers | | 25 | 0.12 | 78.1 | 36 |
| | | 40 | 0.38 | 92.7 | 128 |
| | | 50 | 0.61 | 98.2 | 560 |
| | | 60 | 0.77 | 98.5 | 668 |
| | | 70 | 0.87 | 98.5 | 674 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 3 double layers 3 wk later | | 25 | 0.07 | 98.6 | 711 |
| | | 40 | 0.16 | 98.8 | 800 |
| | | 50 | 0.33 | 98.6 | 738 |
| | | 60 | 0.48 | 98.7 | 783 |
| | | 70 | 0.65 | 98.7 | 776 |

## A6. The separation performance of the composite polyelectrolyte pervaporation membrane with 2 self-assembled double layers in temperature cycling processes

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| | 23 | 0.55 | 97.6 | 416 |
| | 40 | 1.11 | 98.1 | 525 |
| | 50 | 1.32 | 98.4 | 640 |
| Hydrolysis conditions: | 60 | 1.71 | 98.4 | 635 |
| 75$^{O}$C and 20 min | 70 | 1.94 | 98.4 | 624 |
| 2 double layers | 70 | 1.84 | 98.6 | 705 |
| Cycle 1 | 60 | 1.14 | 98.4 | 614 |
| | 50 | 0.72 | 98.2 | 560 |
| | 40 | 0.43 | 97.4 | 382 |
| | 25 | 0.25 | 97.4 | 374 |
| | 26 | 0.31 | 85.0 | 56 |
| | 40 | 0.60 | 89.6 | 87 |
| | 50 | 0.80 | 91.5 | 108 |
| Hydrolysis conditions: | 60 | 1.12 | 93.1 | 135 |
| 75$^{O}$C and 20 min | 70 | 1.33 | 93.3 | 141 |
| 2 double layers | 70 | 1.21 | 93.6 | 148 |
| Cycle 2 | 60 | 0.85 | 92.1 | 117 |
| | 50 | 0.60 | 92.0 | 115 |
| | 40 | 0.37 | 91.8 | 113 |
| | 28 | 0.21 | 91.6 | 110 |
| | 23 | 0.21 | 78.5 | 36 |
| | 40 | 0.46 | 87.0 | 67 |
| | 50 | 0.69 | 91.2 | 104 |
| Hydrolysis conditions: | 60 | 0.97 | 90.4 | 94 |
| 75$^{O}$C and 20 min | 70 | 1.07 | 86.9 | 67 |
| 2 double layers | 70 | 1.01 | 86.7 | 66 |
| Cycle 3 | 60 | 0.86 | 86.3 | 63 |
| | 50 | 0.57 | 86.1 | 62 |
| | 40 | 0.34 | 85.6 | 60 |
| | 26 | 0.18 | 85.3 | 58 |

## A7. The separation performance of a composite polyelectrolyte pervaporation membrane with 3 self-assembled double layers in a temperature cycling process

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m$^{2}$hr) | Water in permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 20 min 3 double layers | 25 | 0.12 | 78.1 | 36 |
| | 40 | 0.38 | 92.7 | 128 |
| | 50 | 0.61 | 98.2 | 560 |
| | 60 | 0.77 | 98.5 | 668 |
| | 70 | 0.87 | 98.5 | 674 |
| | 60 | 0.62 | 98.5 | 645 |
| | 50 | 0.47 | 97.3 | 365 |
| | 40 | 0.22 | 97.5 | 392 |
| | 25 | 0.09 | 97.4 | 380 |

## A8. The effects of the hydrolysis time and hydrolysis temperature on the separation performance of the composite polyelectrolyte pervaporation membranes

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m$^{2}$hr) | Water in Permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 10 min 3+7 double layers Feed: 9.78. 9.69 | 24 | 0.50 | 75.6 | 28 |
| | 40 | 0.83 | 85.0 | 52 |
| | 50 | 1.17 | 88.0 | 68 |
| | 60 | 1.29 | 87.1 | 62 |
| | 70 | 1.53 | 90.4 | 87 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 3+7 double layers | 28 | 0.60 | 97.5 | 350 |
| | 40 | 0.66 | 97.8 | 400 |
| | 50 | 0.77 | 99.6 | 2560 |
| | 60 | 1.02 | 97.7 | 391 |
| | 70 | 1.58 | 98.1 | 472 |
| Hydrolysis conditions: 75$^{O}$C and 30 min 3+7 Double layers | 26 | 0.35 | 96.8 | 265 |
| | 40 | 0.39 | 96.6 | 245 |
| | 50 | 0.42 | 96.5 | 236 |
| | 60 | 0.46 | 95.6 | 186 |
| | 70 | 0.48 | 95.8 | 198 |
| Hydrolysis conditions: 80$^{O}$C and 20 min 4 double layers | 25 | 0.09 | 98.9 | 784 |
| | 40 | 0.18 | 99.1 | 926 |
| | 50 | 0.29 | 99.8 | 3832 |
| | 60 | 0.40 | 99.8 | 3832 |
| | 70 | 0.52 | 99.8 | 3832 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 4 double layers | 25 | 0.16 | 98.7 | 783 |
| | 40 | 0.43 | 99.8 | 4463 |
| | 50 | 0.60 | 99.8 | 4463 |
| | 60 | 0.75 | 99.8 | 4463 |
| | 70 | 0.81 | 98.8 | 843 |
| Hydrolysis conditions: 70$^{O}$C and 20 min 4 Double Layers | 25 | 0.23 | 86.4 | 64 |
| | 40 | 0.51 | 93.7 | 150 |
| | 50 | 0.72 | 95.6 | 218 |
| | 60 | 0.85 | 95.4 | 209 |
| | 70 | 0.98 | 96.1 | 252 |

## A9. The effects of the type of polyelectrolytes on the separation performance of the composite polyelectrolyte pervaporation membranes

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m$^2$hr) | Water in Permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 20 min 3+7 double layers PEI +PAAc | 28 | 0.60 | 97.5 | 350 |
| | 40 | 0.66 | 97.8 | 400 |
| | 50 | 0.77 | 99.6 | 2560 |
| | 60 | 1.02 | 97.7 | 391 |
| | 70 | 1.58 | 98.1 | 472 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 3+7 double layers PDADMAC+PAAc | 25 | 1.08 | 59.5 | 11 |
| | 40 | 1.67 | 69.8 | 18 |
| | 50 | 2.25 | 72.7 | 21 |
| | 60 | 3.01 | 75.4 | 24 |
| | 70 | 4.12 | 78.2 | 29 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers PEI+PAAc | 25 | 0.57 | 90.8 | 99 |
| | 40 | 0.97 | 99.1 | 1094 |
| | 50 | 1.21 | 99.1 | 1142 |
| | 60 | 1.43 | 98.9 | 924 |
| | 70 | 1.65 | 99.8 | 4463 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Chitosan+PAAc | 25 | 0.78 | 69.5 | 23 |
| | 40 | 1.32 | 71.1 | 24 |
| | 50 | 1.87 | 75.5 | 31 |
| | 60 | 2.47 | 80.4 | 41 |
| | 70 | 2.72 | 83.8 | 52 |

## A10. The effect of the molecular weight on the separation performance of composite polyelectrolyte pervaporation membranes

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m2hr) | Water in Permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 20 min 4 double layers PAA 250,000 | 24 | 0.27 | 28.2 | 3 |
| | 40 | 0.50 | 56.4 | 13 |
| | 50 | 0.74 | 62.0 | 16 |
| | 60 | 0.94 | 66.2 | 19 |
| | 70 | 1.09 | 67.5 | 21 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 4 double layers PAA 1,000,000 | 25 | 0.16 | 98.7 | 783 |
| | 40 | 0.43 | 99.8 | 4463 |
| | 50 | 0.60 | 99.8 | 4463 |
| | 60 | 0.75 | 99.8 | 4463 |
| | 70 | 0.81 | 98.8 | 843 |

## A11. The effects of fabrication conditions on the separation performance of the composite polyelectrolyte pervaporation membranes

| Membrane Sample | Temperature ($^{O}$C) | Flux (kg/m2hr) | Water in Permeate (wt %) | Separation Factor |
|---|---|---|---|---|
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 30 min | 22 | 0.61 | 98.5 | 656 |
| | 40 | 1.22 | 99.8 | 4463 |
| | 50 | 1.57 | 99.8 | 4463 |
| | 60 | 1.87 | 99.8 | 4463 |
| | 70 | 1.99 | 99.8 | 4463 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 20 min | 25 | 0.63 | 93.8 | 154 |
| | 40 | 1.22 | 96.1 | 250 |
| | 50 | 1.63 | 96.3 | 261 |
| | 60 | 1.81 | 96.3 | 262 |
| | 70 | 1.97 | 96.3 | 263 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 80$^{O}$C | 25 | 0.65 | 98.5 | 668 |
| | 40 | 1.11 | 99.0 | 958 |
| | 50 | 1.50 | 99.1 | 1094 |
| | 60 | 1.93 | 99.1 | 1176 |
| | 70 | 2.01 | 99.2 | 1213 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 50$^{O}$C | 24 | 0.47 | 94.4 | 169 |
| | 40 | 0.99 | 96.5 | 275 |
| | 50 | 1.34 | 96.7 | 292 |
| | 60 | 1.56 | 96.6 | 290 |
| | 70 | 1.79 | 96.6 | 288 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 25$^{O}$C Post-treatment 1 hr | 25 | 1.24 | 69.0 | 22 |
| | 40 | 2.19 | 60.1 | 15 |
| | 50 | 2.93 | 66.0 | 19 |
| | 60 | 3.87 | 69.5 | 23 |
| | 70 | 4.61 | 67.2 | 20 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 25$^{O}$C Post-treatment 12hr | 25 | 0.64 | 96.3 | 261 |
| | 40 | 1.28 | 97.3 | 360 |
| | 50 | 1.55 | 97.6 | 413 |
| | 60 | 1.88 | 97.9 | 479 |
| | 70 | 2.20 | 98.2 | 540 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 50$^{O}$C Post-treatment 50$^{O}$C | 25 | 0.06 | 78.9 | 37 |
| | 40 | 0.12 | 87.7 | 72 |
| | 50 | 0.35 | 96.5 | 274 |
| | 60 | 0.69 | 97.6 | 409 |
| | 70 | 0.79 | 97.7 | 423 |
| Hydrolysis conditions: 75$^{O}$C and 20 min 2 double layers Deposition 50$^{O}$C Post-treatment 25$^{O}$C | 25 | 0.07 | 70.1 | 23 |
| | 40 | 0.18 | 80.0 | 40 |
| | 50 | 0.60 | 91.6 | 110 |
| | 60 | 0.76 | 91.9 | 115 |
| | 70 | 0.87 | 91.5 | 109 |

| | | | | |
|---|---|---|---|---|
| Hydrolysis conditions: | 27 | 0.63 | 99.8 | 4463 |
| 75$^{O}$C and 20 min | 40 | 1.21 | 99.8 | 4463 |
| 2 double layers | 50 | 1.45 | 99.8 | 4463 |
| Post-treatment 50$^{O}$C, 12 hr | 60 | 1.70 | 99.8 | 4463 |
| Deposition 20 min | | | | |
| shaking/5min | 70 | 1.88 | 99.8 | 4463 |
| Hydrolysis conditions: | 25 | 0.63 | 93.8 | 154 |
| 75$^{O}$C and 20 min | 40 | 1.22 | 96.1 | 250 |
| 2 double layers | 50 | 1.63 | 96.3 | 261 |
| Post-treatment 50$^{O}$C, 12 hr | 60 | 1.81 | 96.3 | 262 |
| Deposition 20 min | | | | |
| No shaking | 70 | 1.97 | 96.3 | 263 |
| | 25 | 0.59 | 99.3 | 1464 |
| | 40 | 0.91 | 99.2 | 1194 |
| Fresh deposition solution | 50 | 1.04 | 99.1 | 1159 |
| | 60 | 1.20 | 98.9 | 947 |
| | 70 | 1.41 | 99.0 | 958 |
| | 25 | 0.64 | 98.2 | 536 |
| | 40 | 1.06 | 98.3 | 581 |
| | 50 | 1.35 | 98.1 | 529 |
| Reused deposition solution | 60 | 1.50 | 97.6 | 407 |
| | 70 | 1.77 | 97.0 | 330 |

## A12. The comparison of separation performance of some composite pervaporation membranes

| Membrane sample | Water in feed (wt %) | Flux ($kg/m^2hr$) | Water in permeate (wt %) |
|---|---|---|---|
| GFT (@ $60^OC$) | 10.0 | 0.20 | 92.0 |
| | 15.0 | 0.35 | 96.0 |
| | 20.0 | 0.50 | 96.5 |
| | 25.0 | 0.70 | 96.5 |
| | 30.0 | 1.00 | 95.5 |
| This work (@$25^OC$) | 8.6 | 0.31 | 95.4 |
| | 14.1 | 0.62 | 97.8 |
| | 20.0 | 0.83 | 99.3 |
| | 24.1 | 0.94 | 99.5 |
| | 27.8 | 1.01 | 99.6 |
| | 32.2 | 1.03 | 99.7 |
| This work (@$60^OC$) | 6.8 | 0.82 | 93.5 |
| | 9.1 | 1.32 | 95.8 |
| | 11.5 | 1.58 | 96.5 |
| Meier (@$50^OC$) | 10.0 | 0.10 | 92.0 |
| | 15.0 | 0.20 | 98.0 |
| | 20.0 | 0.25 | 99.0 |
| | 25.0 | 0.32 | 99.0 |
| | 30.0 | 0.40 | 99.0 |
| Tieke (@$58.5^OC$) | 10.0 | 0.70 | 99.0 |
| | 15.0 | 1.00 | 99.5 |
| | 20.0 | 1.30 | 99.5 |
| | 25.0 | 1.40 | 99.5 |
| | 30.0 | 1.50 | 99.5 |

## A13. Normal probability plots

1. Put all effects and interactions in order according to their values
2. There are altogether 7 effects and interactions
3. Use l/(n+1) to calculate cumulative frequency
4. Obtain the expected normal value
5. Plot with effects and interactions Vs expected normal value

| | Effect of water in permeate @ 25°C | Effect of flux @ 25°C | Effect of water in permeate @70°C | Effect of flux @ 70°C | Probability | Z value |
|---|---|---|---|---|---|---|
| 1 | -17.545 | -0.32 | -14.5675 | -0.685 | 0.125 | -1.1503 |
| 2 | -14.79 | -0.16 | -14.0125 | -0.495 | 0.25 | -0.6745 |
| 3 | -14.595 | -0.1075 | -13.6325 | -0.475 | 0.375 | -0.3186 |
| 4 | 13.94 | -0.018 | 13.4875 | -0.215 | 0.5 | 0 |
| 5 | 14.71 | 0.0525 | 13.6775 | -0.105 | 0.625 | 0.3186 |
| 6 | 17.67 | 0.1625 | 15.0425 | 0.195 | 0.75 | 0.6745 |
| 7 | 18.785 | 0.29 | 15.8525 | 0.445 | 0.875 | 1.1503 |